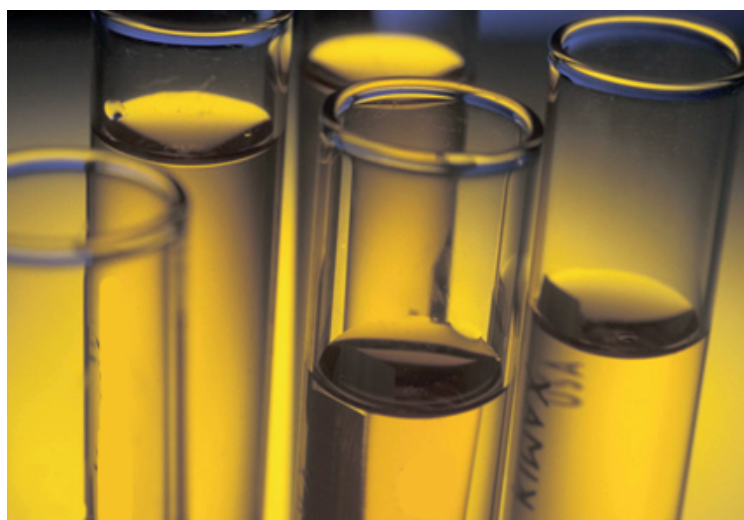


# Module 7

## Organic Chemistry 2



Prepared by Dr. George L. Mhehe



African Virtual university  
Université Virtuelle Africaine  
Universidade Virtual Africana



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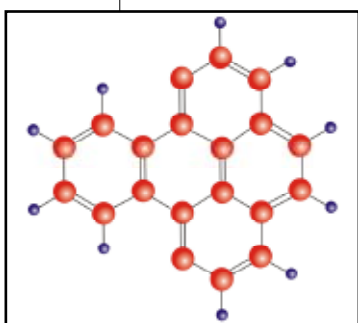
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## I. Module 7, Organic Chemistry 2

By Dr. George L. Mhehe, Open University of Tanzania

### Aromatic compounds and Heterocyclics



## II. Prerequisite Courses or Knowledge

Module 2 unit 4, introduction to organic chemistry

Modules 5 and 6: Organic chemistry I

## III. Time

To cover this model it will require around 120 hours distributed as follows

|           |        |
|-----------|--------|
| Unit I:   | 20 hrs |
| Unit II:  | 80 hrs |
| Unit III: | 20 hrs |

## IV. Material

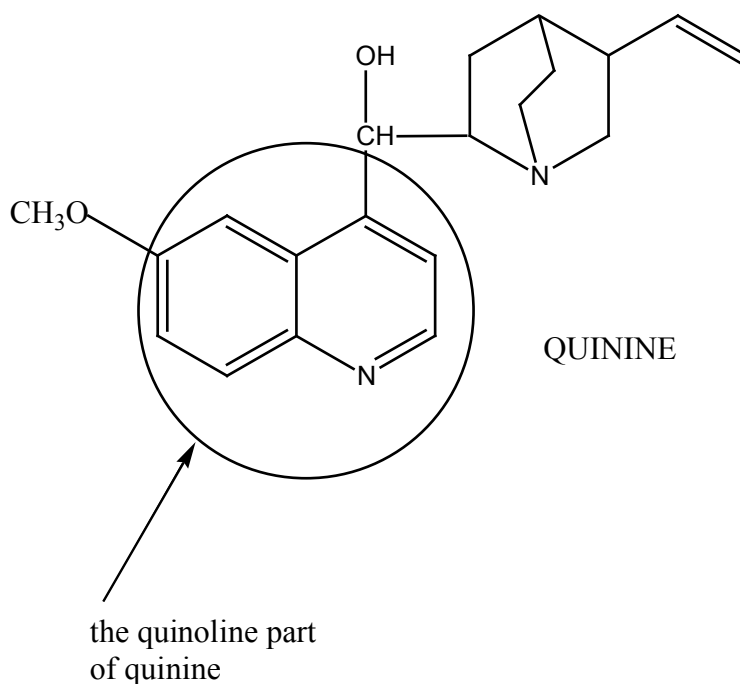
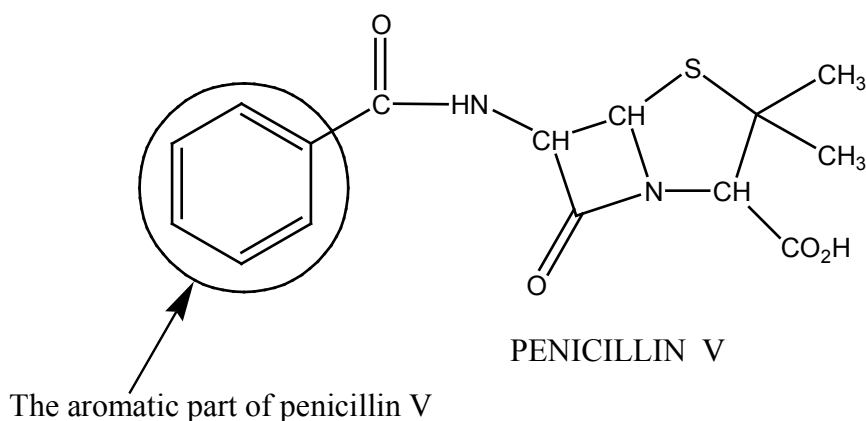
The following are important materials that will be necessary to learn this module:

- Models for structures of aromatic compounds on CD-Rom
- Simulated reactions on CD/Video/DVD
- Animation of reactions on CD/Video/DVD
- Face to face demonstrations using physical models
- Experimental setups for hands-on-experiments involving synthetic reactions of aromatic compounds
- Recommended text books including web-based materials



## V. Module Rationale

Many natural products and many synthetic drugs are partly aromatic. The steroidal hormone estrone, and the well known analgesic morphine have benzenoid aromatic ring components. The tranquilizer diazepam and aspirin for relief of headaches are examples of such drugs. Heterocyclic compounds such as the well known antimalarial, quinine, possess a quinolide structure. It is essential for chemists to study such important molecules that have benzenoid aromatic ring structures. In chemistry, the properties of a substance come from its structure. This module is essentially about the structure, properties and reactions of aromatic hydrocarbons and heterocyclic aromatic compounds.





## VI. Content

### 6.1 Overview

The module deals with the concept of aromaticity and aromatic compounds. It discusses the characteristic properties of aromatic compounds that are based on the benzene ring as the structural unit. The major part of this module therefore discusses the chemistry of benzene and its derivatives.

Components of the module:

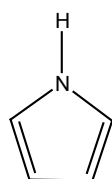
- Aromaticity
- Benzene and its derivatives
- Heterocyclic aromatic compounds

Aromatic compounds and Heterocyclics

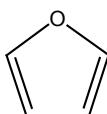
Unit **I** discusses important features that make a compound to be aromatic. Aromatic compounds are cyclic conjugated molecules.

Unit **II**, discusses electrophilic aromatic substitutions of benzene and its derivatives: Halogenation, nitration, sulphonation and Friedel/Crafts reactions.

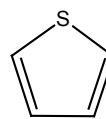
Unit **III**, is on the chemistry of furan, thiophene, pyrrole, and pyridine as representatives of heterocyclic aromatic compounds.



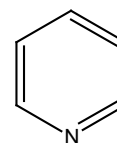
**Pyrrole**



**Furan**



**Thiophene**



**Pyridine**

### 6.2 Outline

Unit I: Aromaticity

- The concept of aromaticity
- how to identify an aromatic compound from its structure

Unit II Benzene and its derivatives

- Benzene as a typical example of an aromatic compound
- structure of benzene



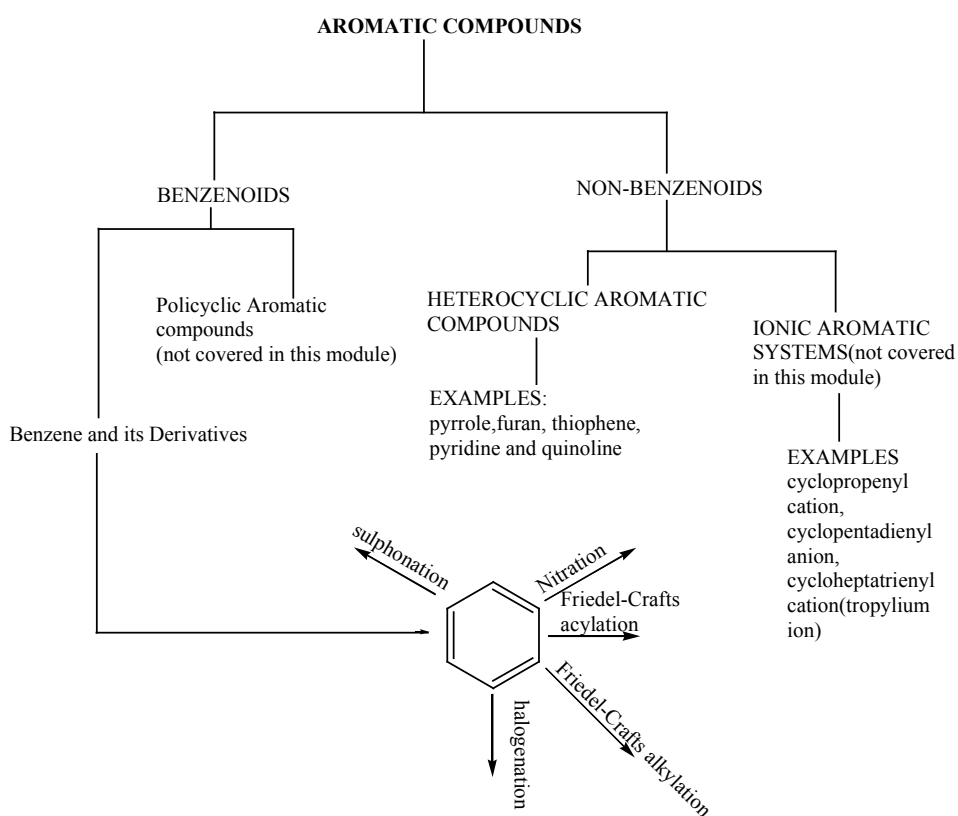
- stability of benzene
- Electrophilic aromatic substitution reactions of benzene and its derivatives
- Effects of substituents on reactivity and orientation of in-coming group

### Unit III: Heterocyclic aromatic Compounds

Definition of a heterocyclic compound

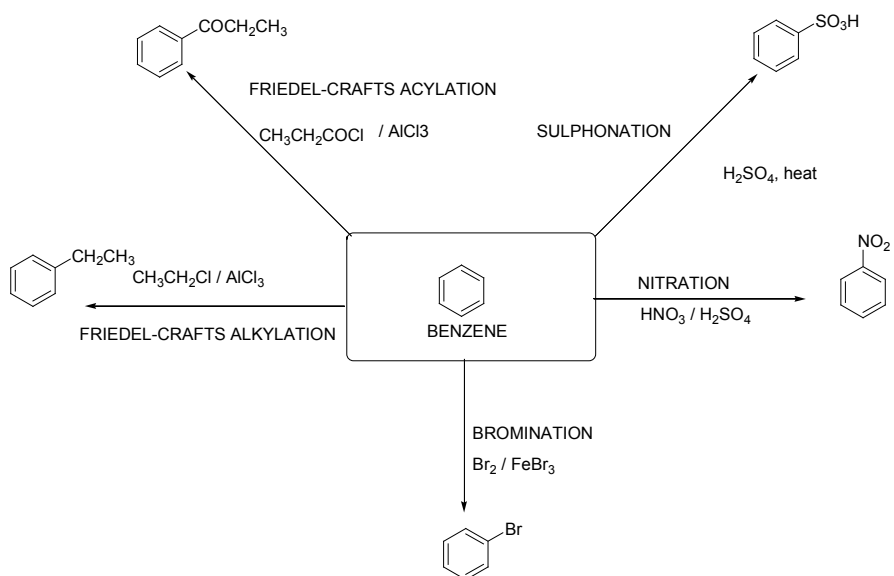
Typical examples of heterocyclic aromatic compounds

Furan, thiophene, and pyrrole as examples of 5-member ring aromatic monoheterocyclics, Pyridine and quinoline Electrophilic aromatic substitution reactions of furan, thiophene and pyrrole





## TYPICAL ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS OF BENZENE





## VII. General Objective(s)

The general objective of this module are:

- to familiarise you with the concept of aromaticity and aromatic compounds so that you are able to identify aromatic compounds based on their structure. The emphasis will be mostly on the chemistry of benzene as the main representative of aromatic compounds and its derivatives.
- to introduce you to electrophilic aromatic substitution reactions of benzene and its derivatives as opposed to addition reactions. These include nitration, halogenation, sulphonation, and Friedel-Crafts alkylation and acylation reactions. These are the typical reactions of benzene and its derivatives.
- to expose you to the structure and chemistry of the heterocyclic systems, furan, thiophene and pyrrole as five-member ring heterocyclics, as well as pyridine and quinoline-which are six member ring heterocyclics.
- to help you to use ICT facilities in teaching



## VIII. Specific Learning Objectives (Instructional Objectives)

### Unit I: Aromaticity

At the end of this unit you should be able to

- (a) define the concept of aromaticity
- (b) identify an aromatic molecule given its structure
- (c) give an argument in favour of the Kekulé structure of benzene.

### Unit II Benzene and its derivatives

At the end of this unit you should be able to:

- (a) write structural formulas for possible isomers and to distinguish formulas for isomers from formulas that represent mono- and di-substituted benzene derivatives
- (b) name different benzene derivatives using the IUPAC system of nomenclature



- (c) write balanced equations involving electrophilic aromatic substitution reactions of benzene and its derivatives
- (d) solve qualitative chemistry problems related to the effect of different substituents present in the benzene ring
- (e) perform simple exercises involving the syntheses of benzene derivative organic compounds

### **Unit III: Furan, thiophene, pyrrole and pyridine**

At the end of this unit you should be able to:

- (a) define a heterocyclic compound
- (b) identify an aromatic heterocyclic molecule based on its structure
- (c) know the preferred positions for electrophilic aromatic substitution in furan, pyrrole, pyridine and thiophene.
- (d) predict and name electrophilic aromatic substitution products of furan, pyrrole, thiophene, and pyridine



## IX. Pre-assessment

### Title of Pre-assessment :

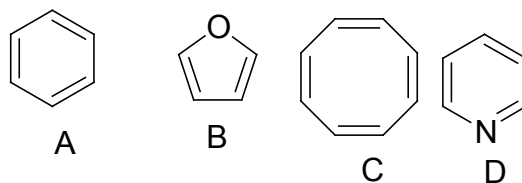
This pre-assessment multiple choice questions are designed to test what you already know about the concepts covered in the module

### 9.1 Rationale

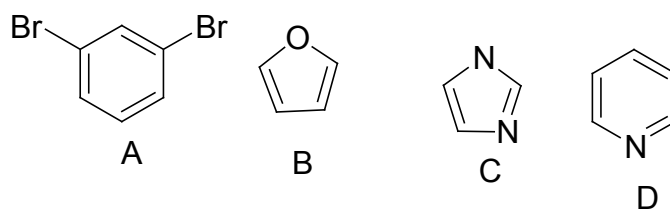
Answering these questions correctly or otherwise will be a good indication of your grasp of the subject matter covered in this module and what you will need to know and be able to use to solve problems.

**Questions :** In each of the following multiple choice questions choose the best answer out of the given options A, B, C or D :

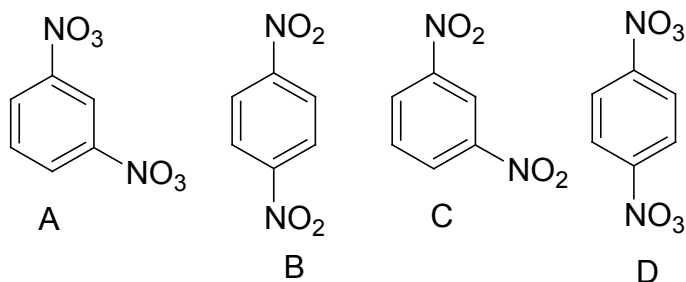
1. Which of these compounds is not aromatic?



2. Which of the given structures represent a diheterocyclic molecule?

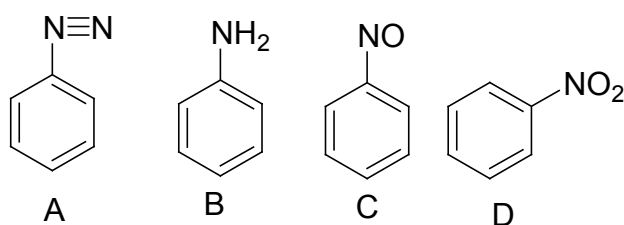


3. Which one of these is the correct structure for m-dinitrobenzene?





4. Which of the following represents the structure of nitrobenzene?



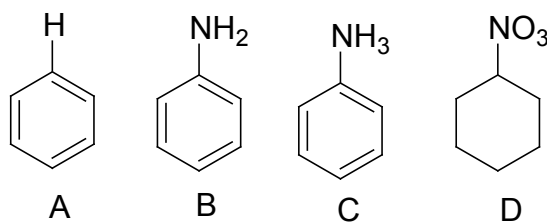
5. The possible number of isomeric monosubstituted benzene derivatives is

- A 2
- B 3
- C 1
- D 6

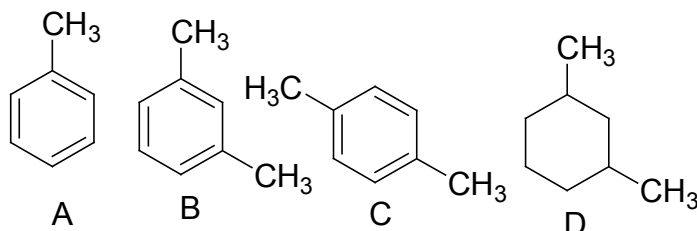
6. The possible number of isomeric disubstituted benzene derivatives is

- A 1
- B 2
- C 3
- D 6

7. When nitrobenzene is reduced using tin (Sn) and HCl the product obtained is

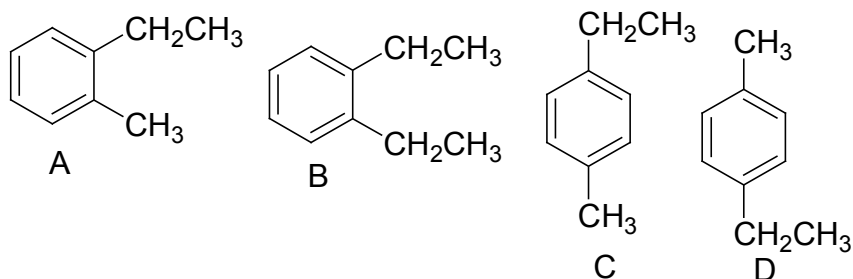


8. The correct structure for m-xylene is





9. The correct structure of o-ethyltoluene is



10. Which one of the following statements is most correct ? Furan is

- A. one of the well known heterocyclic molecule
- B. a five member-ring monoheterocyclic molecule
- C. monoheterocyclic molecule
- D. None of the above

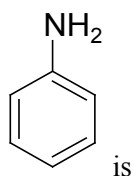
11. The Huckel's  $4n+2$  rule on aromaticity is applicable to

- A. all hydrocarbons
- B. all aromatic hydrocarbons
- C. all aromatic compounds
- D. only naturally occurring aromatic compounds

12. Benzene is

- A. a hydrate of carbon,
- B. a hydrocarbon
- C. a stable aromatic hydrocarbon
- D. a stable hydrocarbon

13. The IUPAC name for the molecule



- A. Pyridine
- B. Aniline
- C. Aminobenzene
- D. Ammonium benzene



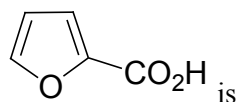
14. Electrophilic aromatic substitution in furan is preferentiallly at position

- A. 3
- B. 1
- C. 2
- D. 4

15. Electrophilic aromatic substitution in pyridine is preferentiallly at position

- A. 1
- B. 3
- C. 4
- D. 2

16. The correct IUPAC name for the molecule



- A. 1-furoic acid
- B. 2-furoic acid
- C. furanylcboxylic acid
- D. 3-furoic acid

17. Oxidation of toluene gives

- A. toluic acid
- B. benzoic acid
- C. benzene carboxylic acid
- D. both B and C are correct answers

18. For a compound to be aromatic it has to be

- A. a complicated cyclic system with  $4n+2$   $\pi$  electrons
- B. conjugated nonplanar molecule
- C. a cyclic conjugated planar molecule
- D. none of the above suffices fully

19. Planarity of a molecule is a necessary condition for aromaticity

- A. true
- B. partially true
- C. false
- D. may be true



20. Benzene and its derivatives typically undergo

- A. addition reactions readily
- B. substitution reaction with difficulty
- C. both substitutions and additions readily
- D. none of the above is true



## 9.2 Answer Key

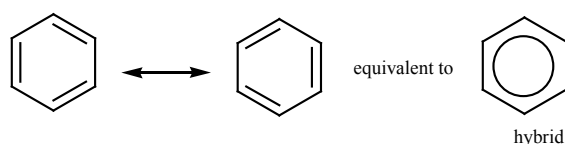
1. C
2. C
3. C
4. D
5. C
6. C
7. B
8. B
9. A
10. B
11. C
12. C
13. C
14. C
15. B
16. B
17. D
18. D
19. A
20. D

**Notes to the student:**

If you get 8 items or more correct you can consider that you are doing fine, but if you get less than 5 items correct then you have to work very hard to pass the course.

**9.3 Pedagogical Comments For Learners****Important Tips:**

- Aromatic hydrocarbons (benzene and other arenes) are stable molecules that hardly undergo addition reactions that are typical of the other unsaturated aliphatic hydrocarbons ( alkenes and alkynes). If aromatic compounds undergo reactions then they do so by substitution reactions rather than addition reactions
- Aromatic hydrocarbons resist reactions that would disrupt their structure so as to retain the  $4n+2$   $\pi$ -electron system
- The stability of benzene (and other arenes) is based on the fact that it exists as a resonance stabilized system with its structure represented as a hybrid of two Kekulé structures:



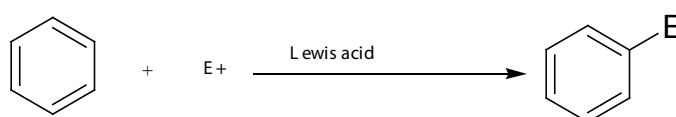


## X. Key Concepts (Glossary)

**Aromaticity:** This refers to the properties of benzene and its derivatives that reflect its special stability. (which resist reactions that would disrupt their structure and thus maintain their unusual stability)

**The  $4n+2$  Huckels Rule:** This refers to the number of  $\pi$ -electrons a compound must have for it to qualify as an aromatic compound, where  $n$  is an integer

**Electrophilic aromatic substitution reaction(s):** This refers to a fundamental reaction type exhibited by aromatic compounds. The general reaction can be represented as:



Where  $E^+$  is an electrophile (electron deficient species)

There are a variety of substitution reactions undergone by nearly all aromatic rings; these include reactions such as nitration, sulphonation, halogenation, and Friedel-Crafts alkylations and acylations.

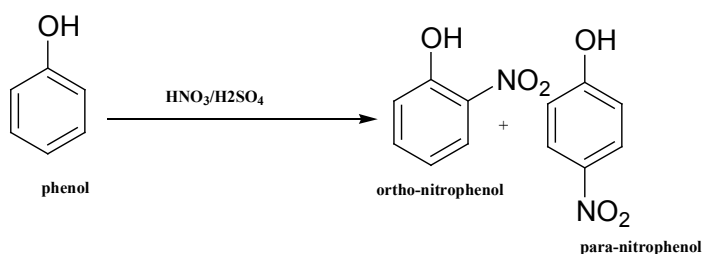
**Friedel-Crafts alkylation reaction:** This is an electrophilic aromatic substitution in which an aromatic compound reacts with an alkyl halide in the presence of aluminium halide to introduce an alkyl group into the benzene/aromatic ring

**Friedel-Crafts acylation reaction:** This is an electrophilic substitution reaction in which an aromatic compound reacts with an acid halide in the presence of aluminium halide or ferric halide to introduce an acyl ( $\text{CH}_3\text{CO}-$ ) group into the benzene/aromatic ring

**Nitration:** This is an electrophilic substitution reaction in which an aromatic compound reacts with a mixture of sulphuric acid and nitric acid to introduce a nitro group ( $\text{NO}_2$ ) into the benzene/aromatic ring

**Halogenation:** This is an electrophilic aromatic substitution reaction in which an aromatic compound reacts with a halogen in presence of aluminium halide or ferric halide to introduce a chloro, bromo or fluoro atom into the benzene/aromatic ring

**Orientation:** refers to the position in the benzene ring where an incoming group would go with respect to an already present substituent in the ring. i.e whether it would go to the ortho/para position or meta position to the present substituent  
eg





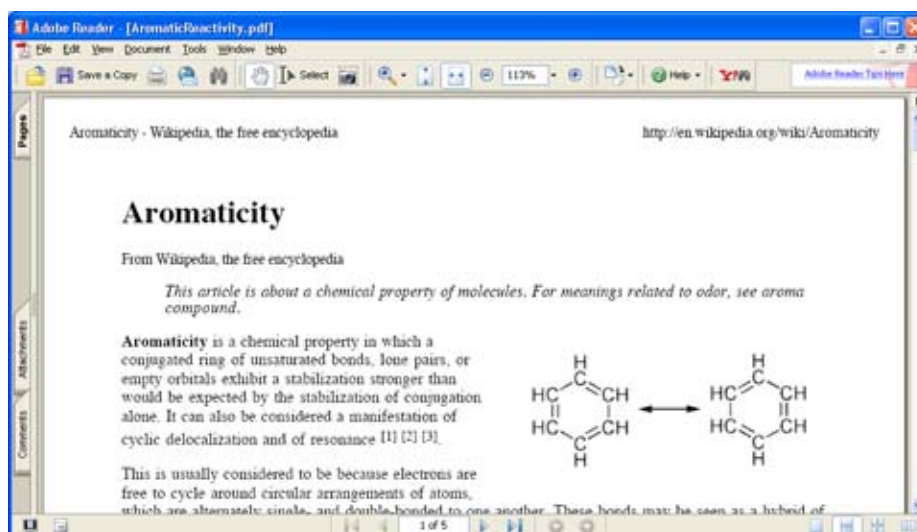
Most **activating** groups are **ortho-para directors**, and most **deactivating** groups are **meta directors** (except the **halogens** which are **deactivating ortho-para directors**)



## XI. Compulsory Readings

### Reading #1

**Complete reference :** Aromaticity: <http://en.wikipedia.org/wiki/Aromaticity>  
6th September 2006 also see the screen capture below: Aromaticity- Wikipedia, the free encyclopedia



**Abstract :** A brief but important discussion on the concept of aromaticity. The discussion is centred around the Kekulé model of the structure of benzene in which benzene is considered a hybrid of two structures with alternating single and double bonds. The article gives in a summary form the characteristics of aromatic compounds.

**Rationale:** The article will help you to study the major characteristics of aromatic compounds and prepare you better to attempt questions on aromaticity.

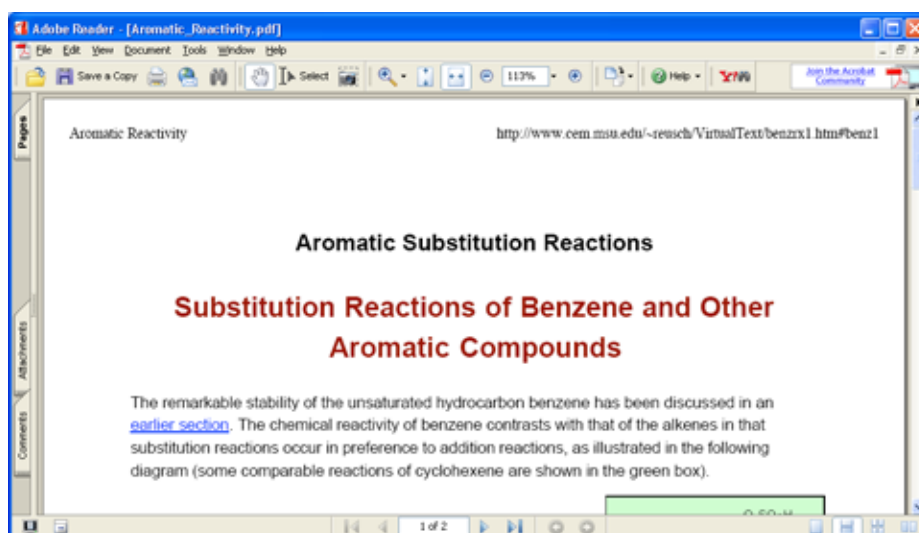


## Reading #2

**Complete reference:** Benzene: From Wikipedia, the free encyclopedia

<http://en.wikipedia.org/wiki/benzene> 6th September 2006

Substitution Reactions of benzene and other Aromatic compounds (see screen capture below)



**Abstract :** The article mostly deals with the structure of benzene from Kekulé's point of view that it is a resonance stabilized structure whose bonds are neither fully single nor double but intermediate between the two, and that all bond lengths in benzene are equal. The typical reactions of benzene are also highlighted in the article.

**Rationale:** Although the article does not provide a comprehensive coverage of benzene and its reactions, it is enough to stimulate further reading for a more detailed understanding of arenes and aromaticity.



## Reading #3

**Complete reference :** From Wikipedia, the free encyclopedia

Pyrrole: <http://en.wikipedia.org/wiki/pyrrole>

Furan: <http://en.wikipedia.org/wiki/furan>

Thiophene: <http://en.wikipedia.org/wiki/thiophene>

Pyridine : <http://en.wikipedia.org/wiki/pyridine>

**Abstract :** The links above give free wikipedia articles on pyrrole, furan, thiophene and pyridine, discussing their chemistry, physical properties, and uses. There are a number of search engines that will lead you to many other important topics on these heterocyclic molecules. You are advised to follow these links to read more on the chemistry of these important heterocyclics

**Rationale:** Pyrrole, furan and thiophene are three important aromatic heterocyclics that are found in a number of natural products. These are aromatic systems that have reactions similar to benzene in that they undergo substitution reactions. It is therefore important that you learn of their chemistry. You will realize that furan is more reactive than benzene in that it even undergoes Diels-Alder reaction. Going through these articles you will learn quite a good amount of chemistry of other heterocyclic compounds and also follow other suggested web links..



## XII. Compulsory Resources

### Resource #1

**Benzene:** movie file

**Abstract :** The film shows the benzene molecular structure and tries to answer the important question: what is it about benzene that makes it behave so much differently from other unsaturated compounds. We will see from the film that the answer is a simple one-the low reactivity of benzene and its derivatives reflects their special stability. Kekulé was wrong. It remained for 20<sup>th</sup> century electronic theories of bonding to provide insight into why benzene is so stable

**Rationale:** It is important that you see this movie because it demonstrates concepts in more intuitive forms which are rather abstract and normally difficult to understand. Without the movie you would find it difficult to visualize the p-orbitals with their electrons being delocalized within the six carbon atoms.

### Resource #2

**Benzene 3d:** movie file

**Abstract :** This interesting movie shows the structure of benzene in three dimensions. The movie depicts the fully symmetrical benzene molecule. It rotates the molecule to show its three dimensions and its planar structure as well. At one point two of the six carbons are shown in colour, this does not in any way signify that the two are different, it just shows that all the six carbons are equally bonded to the two other carbons and to hydrogen. Probably the two carbons are shown in colour so that one can realize that there has been a rotation of the molecule otherwise it would be difficult to make any distinction.

**Rationale:**

The movie depicts the three dimensional nature of benzene, and so it assists you to get a better understanding of the structure of benzene, its bonding and its planar nature as well as its symmetry.



## Resource #3

**Bromination-benzene:**  
**aromatic electrophilic substitution** a movie file

**Abstract:** The movie shows the acceptable mechanism of the bromination of benzene in a stepwise fashion.

**Step 1.** starts to show the role of the Lewis acid  $\text{AlCl}_3$  to activate the electrophile  $\text{Br}_2$  by polarization of the  $\text{Br}_2$  molecule.

**Step 2.** is electrophilic attack of benzene on bromine to form the intermediate  $\pi$ -complex followed by

**Step 3.** the deprotonation step is to regenerate the aromatic system of benzene ring. Thus bromobenzene is the product of this substitution reaction.

**Rationale:** A good understanding of the mechanism shown in this movie is going to be the basis of understanding all the other electrophilic aromatic substitution reactions such as sulphonation, nitration alkylation and acylation. The difference is only on the electrophiles used.



## XIII. Useful Links

### Useful Link #1

**Title : Electrophilic substitution reactions**

**URL :**

<http://www.chemguide.co.uk/mechanisms/elsub/halogenation.html>

<http://www.chemguide.co.uk/mechanisms/elsub/nitration.html>

<http://www.chemguide.co.uk/mechanisms/elsub/sulphonation.html>

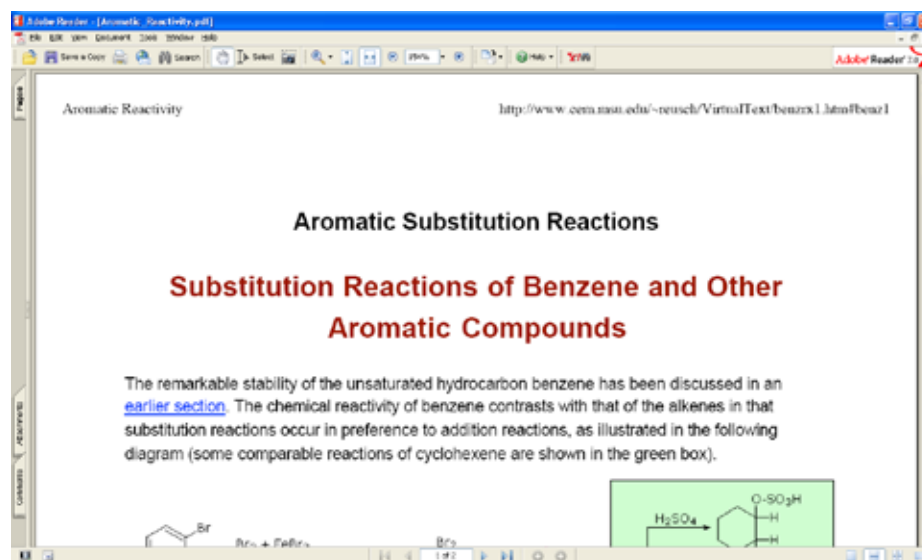
<http://www.chemguide.co.uk/mechanisms/elsub/fcalkyl.html>

<http://www.chemguide.co.uk/mechanisms/elsub/fcacyl.html>

<http://www.chemguide.co.uk/mechanisms/elsub/toluene.html>

(all visited on 14th September 2006)

### Screen capture





electrophilic substitution - the halogenation of benzene - Microsoft Internet Explorer

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Address <http://www.chemguide.co.uk/mechanisms/elsub/halogenation.html>

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## THE HALOGENATION OF BENZENE

This page gives you the facts and a simple, uncluttered mechanism for the electrophilic substitution reaction between benzene and chlorine or bromine in the presence of a catalyst such as aluminium chloride or iron. If you want this mechanism explained to you in detail, there is a link at the bottom of the page.

### The electrophilic substitution reaction between benzene and chlorine or bromine

#### The facts

Benzene reacts with chlorine or bromine in an electrophilic substitution reaction, but only in the presence of a catalyst. The catalyst is either aluminium chloride (or aluminium bromide if you are reacting benzene with bromine) or iron.

Done Internet

electrophilic substitution - the nitration of benzene - Microsoft Internet Explorer

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Address <http://www.chemguide.co.uk/mechanisms/elsub/nitration.html>

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## THE NITRATION OF BENZENE

This page gives you the facts and a simple, uncluttered mechanism for the electrophilic substitution reaction between benzene and a mixture of concentrated nitric acid and concentrated sulphuric acid. If you want the nitration mechanism explained to you in detail, there is a link at the bottom of the page.

### The electrophilic substitution reaction between benzene and nitric acid

#### The facts

Benzene is treated with a mixture of concentrated nitric acid and concentrated sulphuric acid at a temperature not exceeding 50°C. As temperature increases there is a greater chance of getting more than one nitro group, -NO<sub>2</sub>, substituted onto the ring.

Done Internet



electrophilic substitution - the sulphonation of benzene - Microsoft Internet Explorer

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Address <http://www.chemguide.co.uk/mechanisms/elsub/sulphonation.html>

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## THE SULPHONATION OF BENZENE

This page gives you the facts and a simple, uncluttered mechanism for the electrophilic substitution reaction between benzene and sulphuric acid (or sulphur trioxide). If you want this mechanism explained to you in detail, there is a link at the bottom of the page.

### The electrophilic substitution reaction between benzene and sulphuric acid

#### The facts

There are two equivalent ways of sulphonating benzene:

- Heat benzene under reflux with concentrated sulphuric acid for several hours.

Done Internet

electrophilic substitution - the alkylation of benzene - Microsoft Internet Explorer

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Address <http://www.chemguide.co.uk/mechanisms/elsub/fcalkyl.html>

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Links

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- electrophilic substitution in methy...

## THE FRIEDEL-CRAFTS ALKYLATION OF BENZENE

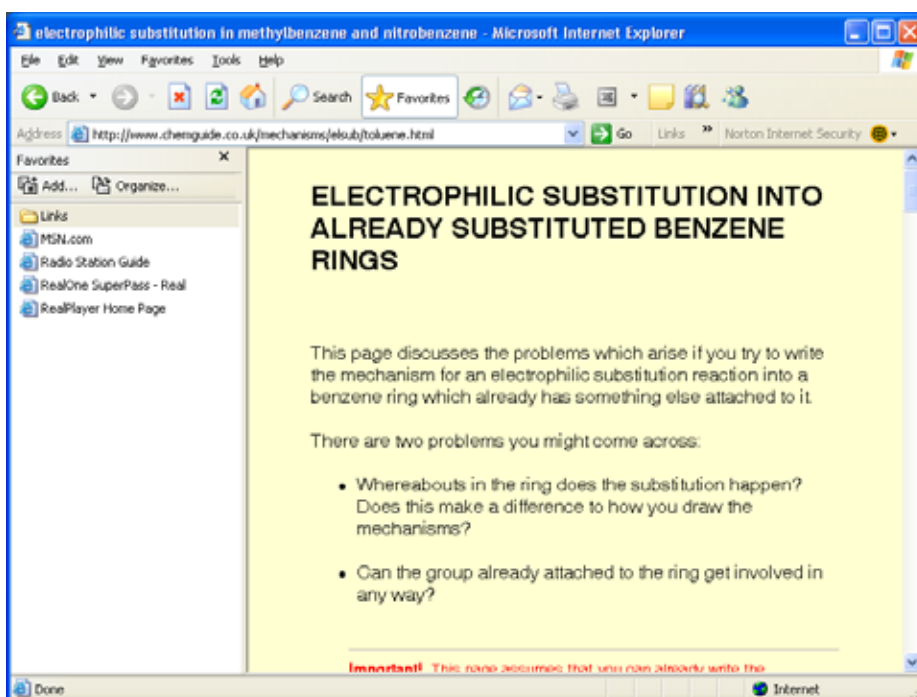
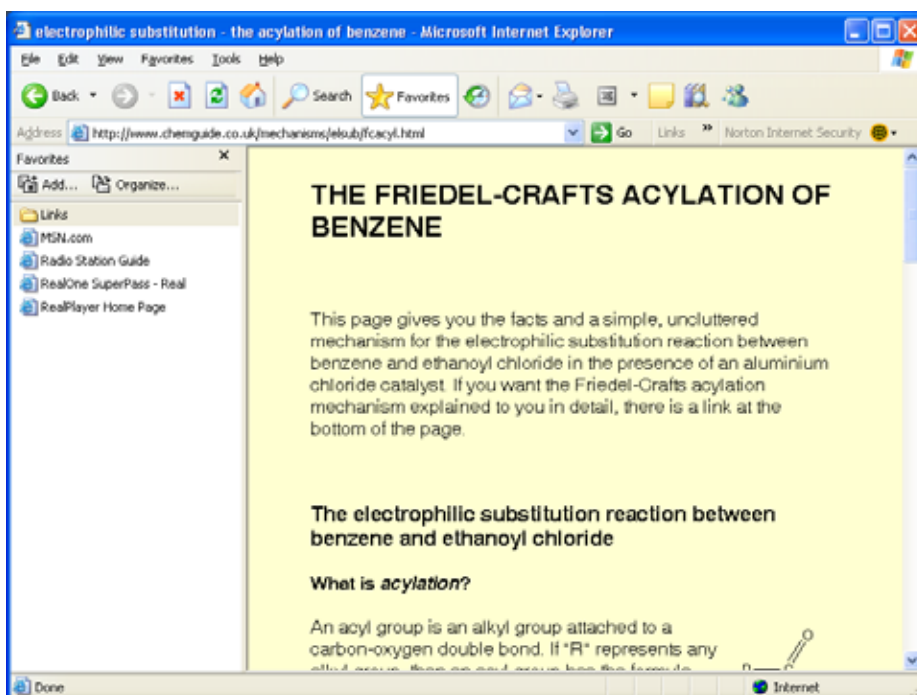
This page gives you the facts and a simple, uncluttered mechanism for the electrophilic substitution reaction between benzene and chloromethane in the presence of an aluminium chloride catalyst. Any other chloroalkane would work similarly. If you want the Friedel-Crafts alkylation mechanism explained to you in detail, there is a link at the bottom of the page.

### The electrophilic substitution reaction between benzene and chloromethane

#### What is alkylation?

Alkylation means substituting an alkyl group into something - in this case into a benzene ring. A hydrogen on the ring is replaced by an alkyl group.

Done Internet



**Description:** Electrophilic substitution reactions are the main reactions of benzene and its derivatives. These are discussed in the articles whose links are given above. Halogenation which can be by bromination or chlorination are typical examples; Nitration which introduces the nitro group, a group which can easily be reduced to



the amino group and then be used in manufacture of azo dyes or be used as nitro derivatives of benzene in pesticides; sulphonation is also an important process in which the sulphonic acid group can be transformed into OH to get phenol which is a very important functional group, the sulphonic acid group itself is also important in the dye industry. The Friedel-Crafts alkylation and acylation reactions are also discussed. In all these reactions the mechanisms are also discussed. Finally there is discussion on substitution reactions of toluene as an example of a substituted benzene undergoing reactions. In this we see the possibility of getting isomeric derivatives of toluene. The aspects which could not be understood from the short compulsory reading can now be understood from these discussions. It is very important that you study these articles. The fact that the methyl group directs an incoming group to the 2, and 4-positions ( **the ortho and para positions** ), the alkyl group in this case the methyl group is an **ortho-para director**. Substitution in nitrobenzene is also discussed and that the nitro group directs an incoming group to the meta position i.e. it is a **meta director**.

**Rationale:** A good understanding of electrophilic substitution reactions, amounts to understanding the chemistry of benzene and its derivatives. All the reactions of benzene follow a very similar pattern mechanistically. This understanding is crucial even in the understanding of the many industrial processes where benzene or its derivatives are used as raw materials.



## Useful Link #2

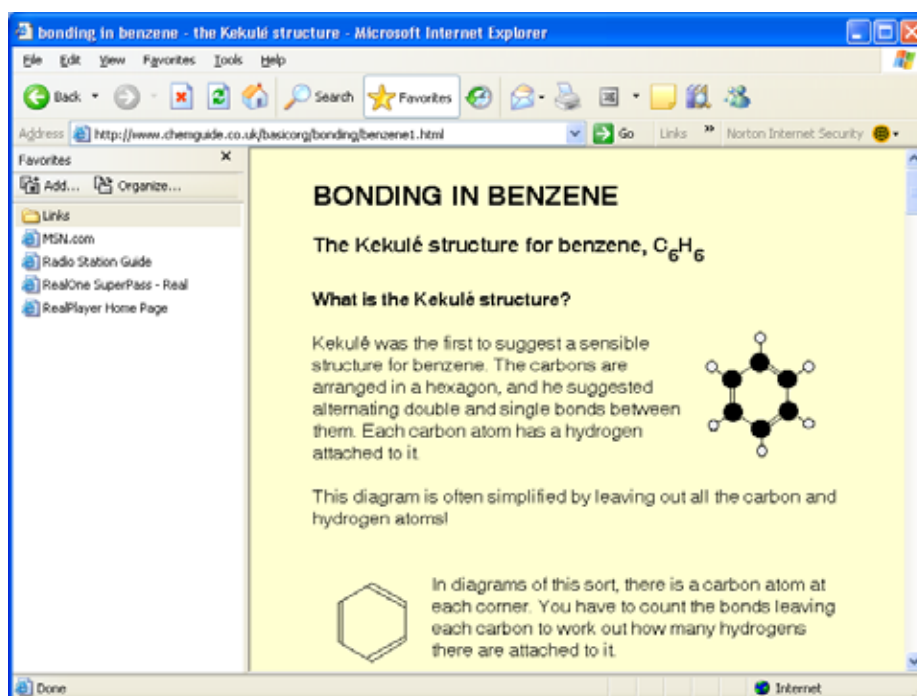
**Title :Bonding in benzene**

**URL :**

<http://www.chemguide.co.uk/basicorg/bonding/benzene1.html>

(visited on 15th September 2006)

**Screen capture :**



**Description:** It discusses the structure of benzene and bonding from kekulé point of view. The structure is given as a hexagon made of six carbons leaving out the hydrogens. The paper discusses the Kekulé structure in terms of its shortcomings pertaining to the chemistry of benzene, the shape of benzene and the unusual stability of benzene.

**Rationale:** A good article which discusses the merits and demerits of the Kekulé proposal of benzene structure.

The concept of bonding in benzene is important but rather complex,. It is therefore important that you get a good grasp of the concept from this and other related articles..

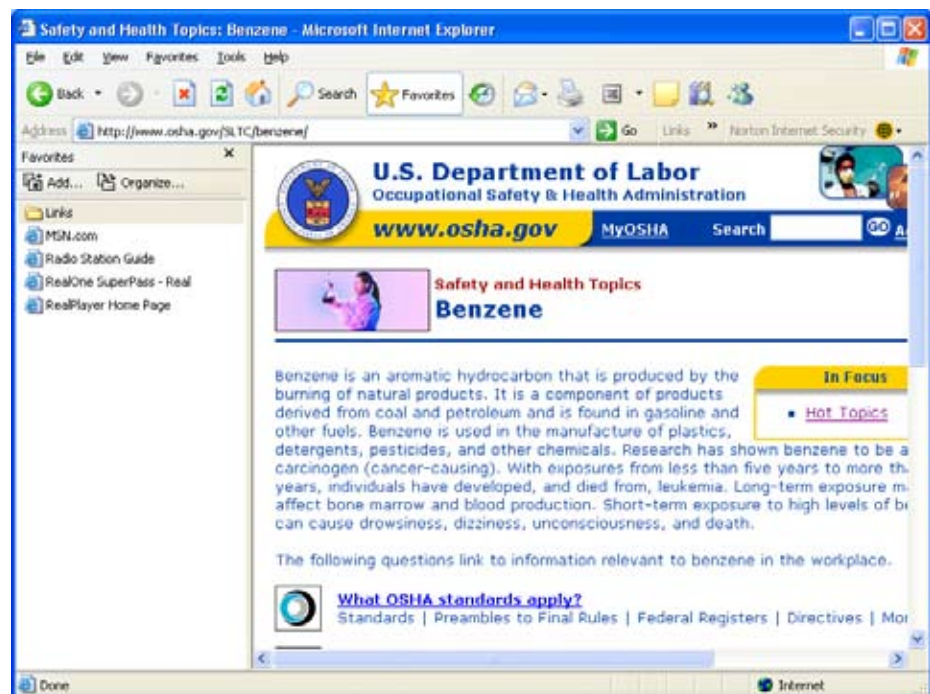


## Useful Link #3

**Title :** benzene-Safety and Health Topics

**URL :** <http://www.osha.gov/SLTC/benzene/>(visited on 15th September 2006)

**Screen capture :**



**Description:** This article gives information on the hazardous nature of benzene. Benzene is harmful to our health because it is carcinogenic and therefore we should handle it with care. We should avoid contact to our skin, our eyes and also we should avoid inhaling it. If we swallow benzene accidentally we should immediately consult a doctor.

**Rationale:** It is important that you know the hazardous nature of the chemicals you deal with. This helps you to know the precautions you should take in case you are to handle it. In industry employers have to know these facts so that they do not expose their workers unnecessarily to the harmful effects of benzene and its compounds.



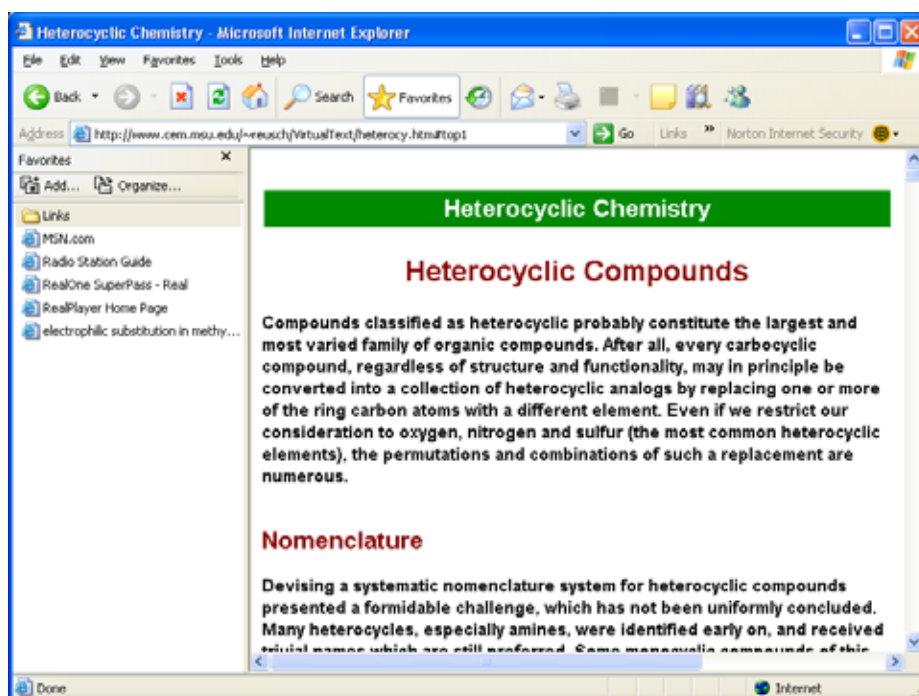
## Useful Link #4

**Title : Heterocyclic compounds**

**URL :**

<http://www.cem.msu.edu/%7Ereusch/VirtualText/heterocy.html>  
(visited on 15th September 2006)

**Screen capture :**



**Description:** Extensive chemistry of heterocyclics including that of pyrrole, furan, thiophene etc. electrophilic aromatic substitution reactions of pyrrole, furan, thiophene are discussed, including their mechanisms. There are also reactions of pyridine to form N-substituted derivatives of pyridine for example N-acetyl pyridinium chloride obtained by reaction of pyridine with acetyl chloride. There are also other lead links that discuss Friedel Crafts reactions of benzene, but for the purpose of this unit you should pay special attention to the chemistry of pyrrole, furan, thiophene and pyridine.

**Rationale:**

The link has a very extensive coverage on chemistry of heterocyclic aromatic compounds, it also covers non aromatic compounds, but for the purpose of this module you should concentrate on the aromatic systems only.



## Useful Link #5

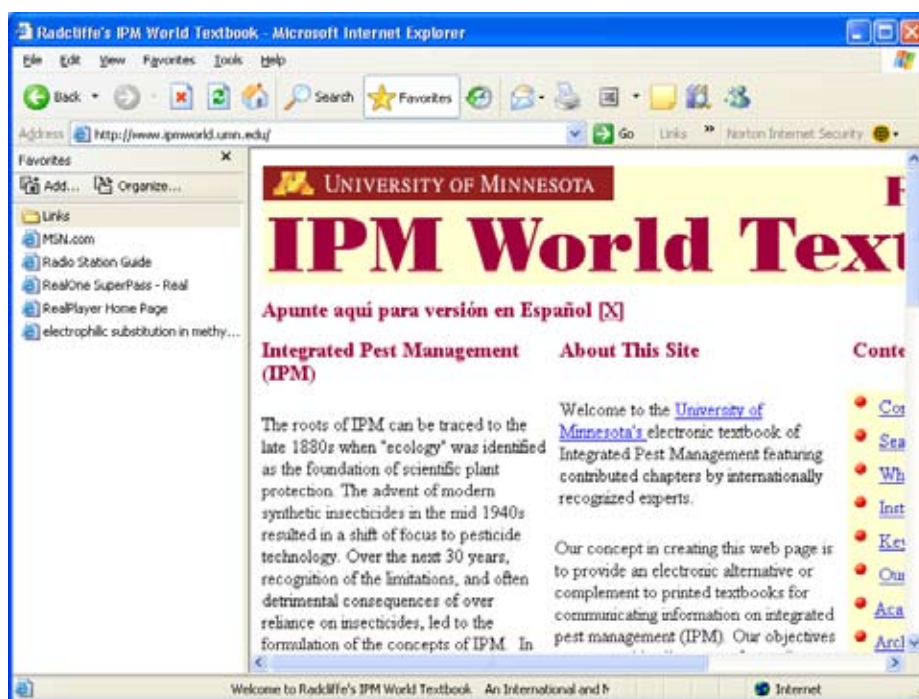
**Title :** Introduction to Insecticides; extract from IPM Textbook Pesticides 6<sup>th</sup> ed. 2004 by George W. Ware and David M. Whitacre, available for online purchase. Publisher: MeisterPro Information

**URL :**

<http://www.ipmworld.umn.edu/>

(visited on 15<sup>th</sup> September 2006)

**Screencapture:**



**Description:** An extensive coverage of pesticide chemistry involving derivatives of benzene as the insecticides, typical application of benzene chemistry in pesticides. It covers organochloro pesticides such as DDT, hexachlorocyclohexane HCH, organophosphate, malathion, carbamates, dinitrophenols and pyrethroids. Structures of many of these pesticides are given. This should give a good reference material on pesticide chemistry.

**Rationale:** Pesticides are important in pest management in general and in agriculture in particular. Many tons of agricultural crops are destroyed by pests. Hence a good understanding of how pesticides are manufactured (from benzene and benzene derivatives) is important for you as a chemistry student to get the feel of the importance of chemistry in our everyday life.



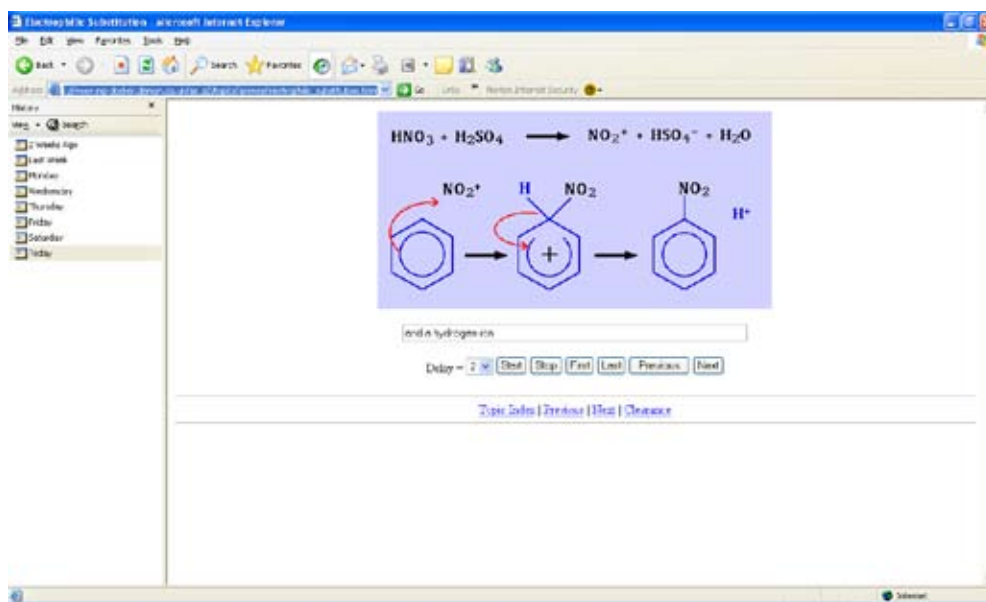
## Useful Link #6

**Title :** Electrophilic substitution-Animation on mechanism of nitration of benzene

**URL :**

[http://www.mp-docker.demon.co.uk/as\\_a2/topics/arenes/electrophilic\\_substitution.html](http://www.mp-docker.demon.co.uk/as_a2/topics/arenes/electrophilic_substitution.html)

**Screen capture :**



**Description:** A very good animation that shows clearly the stepwise mechanism of nitration of benzene to give nitrobenzene. It starts with the generation of the nitrating agent, the nitryl cation ( $\text{NO}_2^+$ ) (also called nitronium ion) from a mixture of nitric acid and sulphuric acid. This is followed by attack of benzene on the nitryl cation to form an unstable intermediate which then breaks down to give the product nitrobenzene and a hydrogen ion  $\text{H}^+$ .

**Rationale:** Mechanism of reactions are difficult aspects in chemistry for students to understand. This animation will be a very good way to make students grasp the concept involved appropriately.



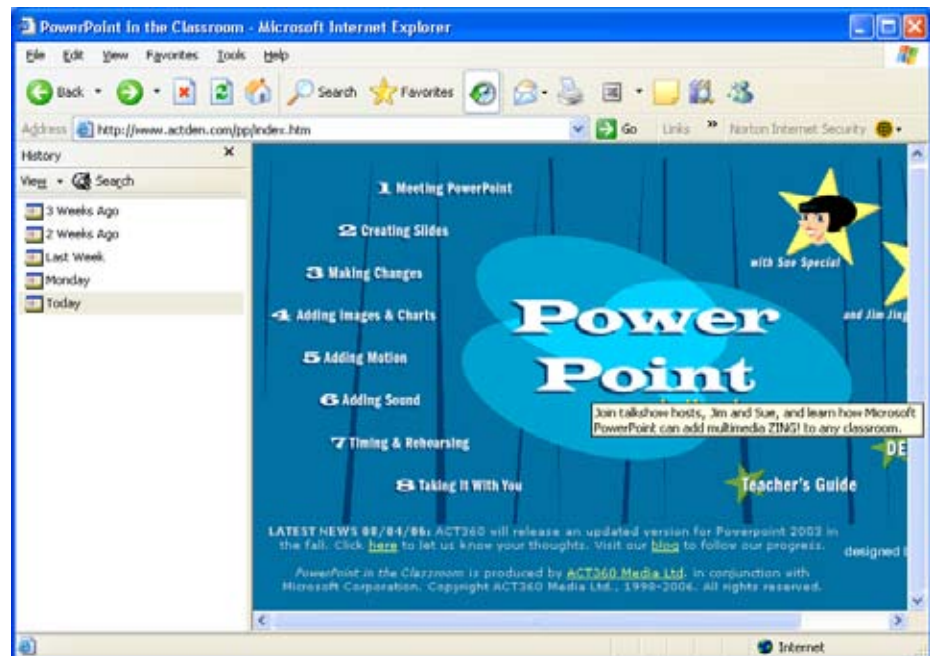
## Useful Link #7

**Title :**Powerpoint in the classroom: creating slides

**URL :**

<http://www.actden.com/pp/index.htm>

**Screen capture :**



**Description:** This gives a good lesson on use of powerpoint as a tool for teaching. It covers the topics: Meeting Powerpoint, creating slides, making changes, adding images and charts , adding motion, adding sound, timing and rehearsing and taking it with you. It is in a form of tutorials that the student teacher can follow and get the necessary knowledge to enable him/her prepare a presentation using powerpoint.

**Rationale:** Powerpoint is a very useful tool in teaching. It makes the presentation interesting to the student . It is therefore important for anyone who intends to teach using ICT facilities to know use of powerpoint.



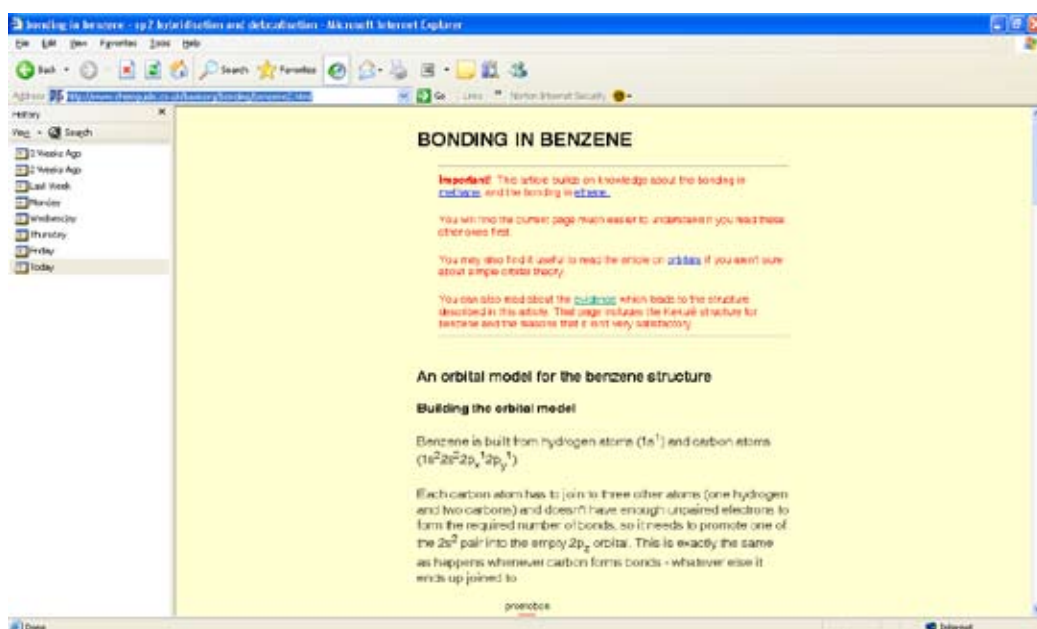
## Useful Link #8

**Title : BONDING IN BENZENE-SP<sup>2</sup> HYBRIDIZATION AND DELOCALIZATION**

URL :

<http://www.chemguide.co.uk/basicorg/bonding/benzene2.html>

Screen capture :



**Description:** This discusses bonding in benzene based on the knowledge gained from bonding in aliphatic compounds like methane and ethene. Thus, the knowledge of electronic configuration of carbon, hybridization of orbitals comes in here. It is therefore important that you revise these concepts so as to follow this discussion better. The article also gives other useful links that can be followed.

**Rationale:** The concept of bonding in benzene is important in order to understand benzene structure and its reactivity. It is important that this is studied thoroughly.



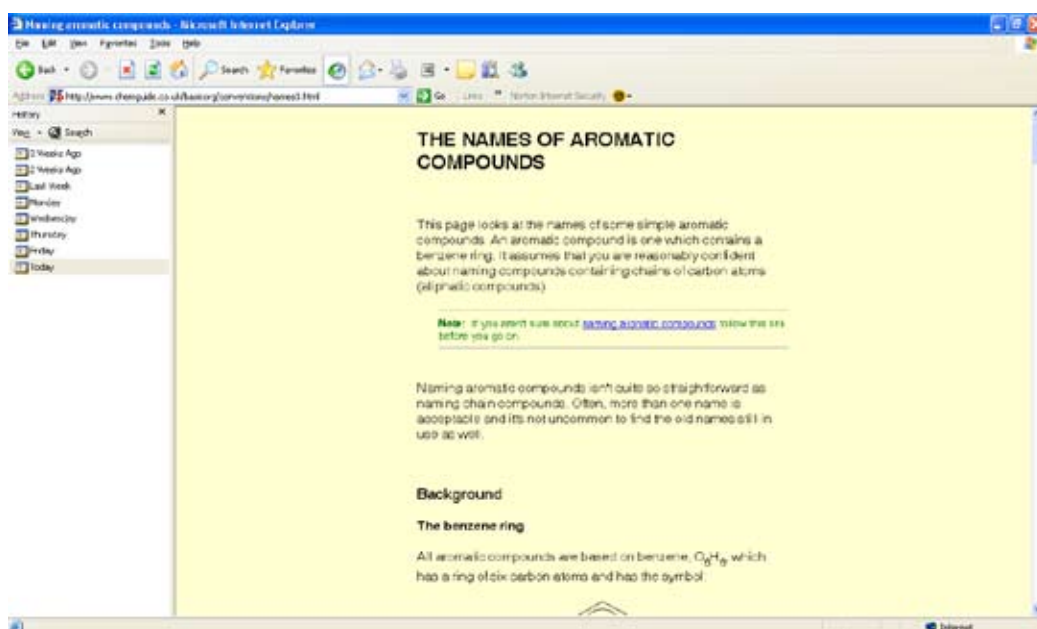
## Useful Link #9

**Title : The Names Of Aromatic Compounds**

**URL :**

<http://www.chemguide.co.uk/basicorg/conventions/names3.html>

**Screen capture :**



**Description:** The article gives a good introduction to nomenclature of aromatic compounds. It gives examples of monosubstituted benzene derivatives as well as disubstituted derivatives. . It also gives some common names which are traditional, not based on the rules discussed in here. It also gives other additional links which lead to nomenclature of other organic compounds.

**Rationale:** The nomenclature of organic compounds is a bit complex, it is therefore important that you follow this introductory discussion on naming organic compounds well, so that as the nomenclature becomes more complicated you will be able to follow it.



## Useful Link #10

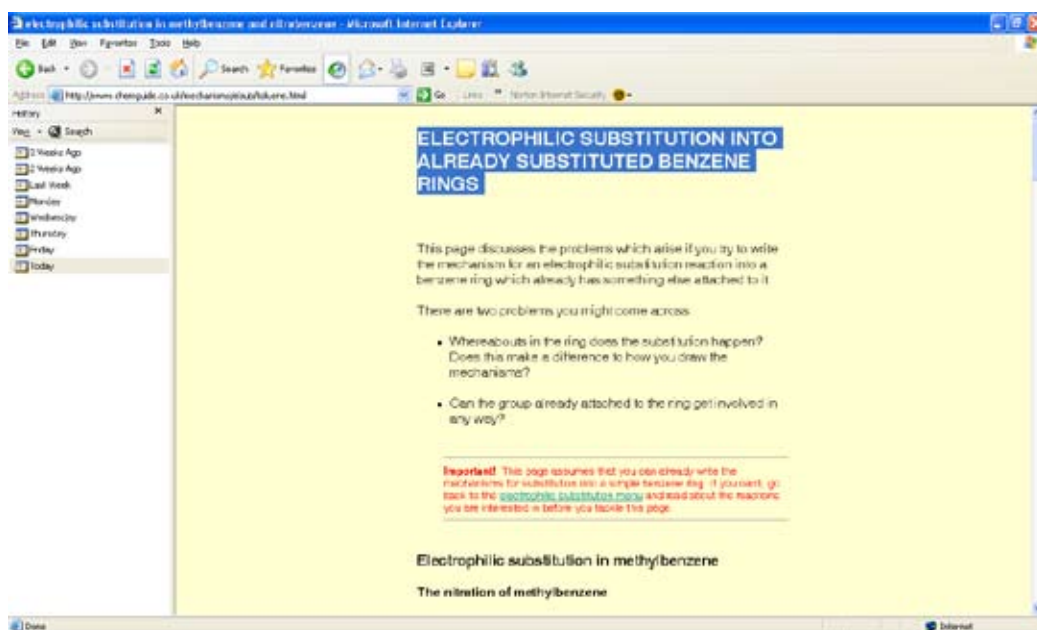
### Title : Electrophilic Substitution Into Already Substituted Benzene Rings

URL :

<http://www.chemguide.co.uk/mechanisms/elsub/toluene.html>

<http://www.chemguide.co.uk/organicprops/arenes/halogenation.html>

Screen capture :



**Description:** This discusses the problems encountered when there is already a group within the benzene ring and we want to introduce another group. The problems are based on:

- Where in the ring will the substitution occur and how is the mechanism affected by the already present group?
- Can the group already present get involved in any way?

A discussion of the effect of different substituents to reactivity and orientation of the incoming group is given. There is also a discussion of the mechanisms of electrophilic aromatic substitution reactions.



**Rationale:** This is a very good site to learn quite a lot on electrophilic aromatic substitution reactions of already substituted benzene rings. A good study of this site plus the other links sited therein will make you be in a good position to attempt successfully many examination questions on this very important topic.



## XIV. Learning Activities

### Title of Learning Activity : Aromatic nature of benzene

#### Summary of the learning activity

Unit I: Aromaticity

At the end of this unit you should be able to:

- (a) define the concept of aromaticity
- (b) give an argument in favour of the Kekulé structure of benzene and show how the other possibilities can be rejected

#### Summary

Aromatic compounds now are benzene and related molecules which are :

- cyclic conjugated molecules
- unusually stable and tend to resist any reaction that would disrupt the conjugated structure
- planar molecules and
- undergo substitution reactions instead of additions which are typical of unsaturated molecules

All aromatic molecules have  $4n+2$   $\pi$ -electrons where  $n$  is an integer. This is the Huckel's  $4n+2$  rule on aromaticity. The structure and stability of benzene is discussed. The main discussion on reactions of benzene appears in unit II. For better understanding of this unit use of multimedia facilities is advocated.

#### Key words

Aromaticity  
Kekule structure  
Conjugated system  
Stability  
 $4n+2$   $\pi$ -electrons

**List of relevant readings**

From Textbook Revolution-Taking the Bite out of Books

**<http://textbookrevolution.org/chemistry/>**

1. Virtual Textbook of Organic Chemistry Organic Chemistry by William Reusch
2. Organic Chemistry by Richard and Sally Daley
3. Organic Chemistry Practice Problems by William Reusch

**List of relevant resources**

1. A computer with internet facility to access links and copywrite free resources
2. Models on CD-Rom for aromatic structures
3. Physical models for structures
4. Multimedia resources like video, teleconferencing, CD-Rom

**List of relevant useful links :**

Textbook Revolution -Taking the Bite out of Books

**<http://textbookrevolution.org/chemistry>**



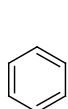
## Detailed description of the activity

### Aromatic Compounds

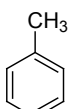
The concept of Aromaticity: benzene and aromaticity

#### Introduction

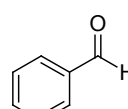
In the early days of organic chemistry the word aromatic was used with a connotation of odour of fragrant substances. This was true at that time because most of the early aromatic compounds were indeed fragrant since they were obtained from natural sources such as balsams, resins or essential oils. Examples of these were benzaldehyde (from cherries, peaches and oil of bitter almonds), benzoic acid and benzyl alcohol (from gum benzoin), toluene (from tolu balsam), and benzene (from coal tar).



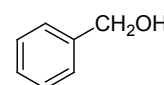
benzene



toluene



benzaldehyde



benzyl alcohol

However, it was soon realized, that substances grouped as aromatic differed from most other organic compounds in their chemical behaviour.

Nowadays we use the term “aromatic”, not in the sense of odour or fragrance but to refer to benzene and its structural relatives-arenes that are much more stable than we expect them to be based on their formulation as conjugated trienes. The association of aromaticity with fragrance has long been abandoned.

Our goal in this module is to develop an appreciation for the concept of aromaticity, to show that aromatic compounds exhibit chemical behaviour quite different from that of the aliphatic compounds covered in earlier modules. Aromatic hydrocarbons are benzene and compounds that resemble benzene in their chemical behaviour. Aromatic properties of benzene are those properties which distinguish it from aliphatic hydrocarbons.

In the nineteenth century, benzene was shown to have the empirical formula  $\text{CH}$ . Later its molecular formula was shown to be  $\text{C}_6\text{H}_6$ . This itself was a rather surprising discovery. Benzene has an equal number of hydrogen atoms as carbon atoms in its molecule while for most compounds the ratio of hydrogen to carbon is much higher, usually twice as many. Benzene with a formula of  $\text{C}_6\text{H}_6$  or with general formula  $\text{C}_n\text{H}_{2n-6}$ , must consist of highly unsaturated molecules. It has an index of hydrogen deficiency (also known as double bond equivalent) equal to four. However, as we will see in this module, benzene and other aromatic compounds are characterized by their tendency to undergo substitution reactions



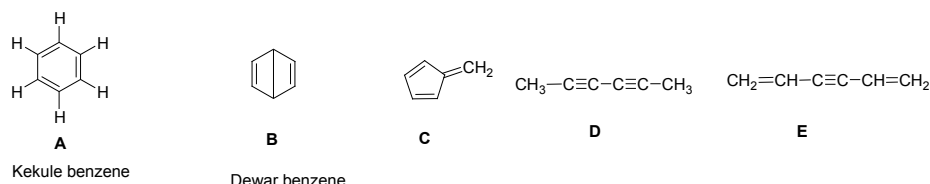
characteristics of saturated compounds rather than addition reactions which are typical of unsaturated compounds.

Kekule was the first man to recognize that early aromatic compounds all contain a six-carbon unit and that they retain this six-carbon unit through most chemical transformations.

### Molecular formula of benzene, Isomer number, and the Kekulé structure of benzene.

From its elemental composition and molecular weight, benzene was known to contain six carbon atoms and six hydrogen atoms. The major question was: how are those atoms arranged? This was a question that was difficult to answer for many years. In middle nineteenth century Kekulé had proposed that the carbon atoms can join to one another to form chains. It was in 1865 that he offered an answer to the question of benzene that those carbon chains can sometimes be closed to form rings.

There are a number of structures which have been proposed and which are consistent with the formula  $C_6H_6$ , a number of them, cyclic as well as acyclic. Some examples of these are:



The following are some important aspects considered in the argument towards the most probable structure of benzene:

### Possible isomer number

(i) Benzene yields only one monosubstitution product  $C_6H_5Z$ . For example only one bromobenzene,  $C_6H_5Br$  is obtained when one hydrogen atom is replaced by bromine, only one chlorobenzene  $C_6H_5Cl$ , and only one nitrobenzene,  $C_6H_5NO_2$  etc. has ever since been made. This implies that each hydrogen in benzene must be equivalent to every other one since the replacement of any one of them gives the same product. Based on this it can be argued that structure **E** must be rejected since it would yield two isomeric monobromo derivatives. Similarly structures **B** and **C** are unsatisfactory and must be rejected.



### Question

How many monosubstitution products would each of structures **B** and **C** yield?

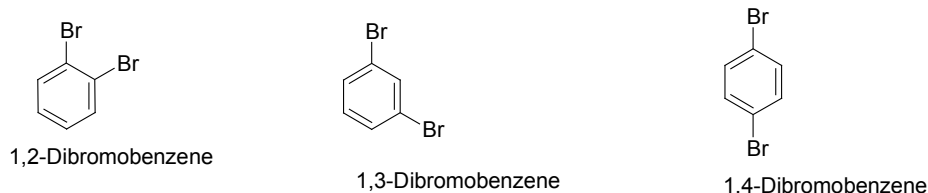
To this point, structures **A** and **D** are still candidates; they qualify the monosubstitution isomer number criterion.

(ii) Benzene yields three disubstitution products,  $C_6H_4YZ$  or  $C_6H_4Z_2$ . Thus, three and only three isomeric dibromobenzenes,  $C_6H_4Br_2$ , three chloronitrobenzenes,  $C_6H_4ClNO_2$  etc. have been made. This fact limits our choice on the possible structure of benzene even further, for example, structure **D** must now be rejected since it fails this test. (Why?). This now leaves us with only **A** as a possibility for the structure of benzene.

### Question

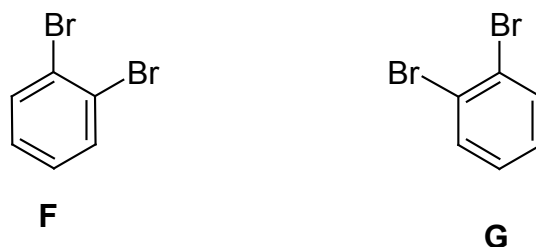
How many disubstitution products would **D** yield?

So far it looks as if structure **A** is consistent with this new fact. For example, we can expect three dibromo derivatives as shown, the 1,2-, the 1,3-, and the 1,4-dibromo compounds.



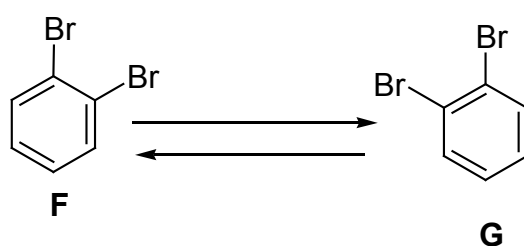
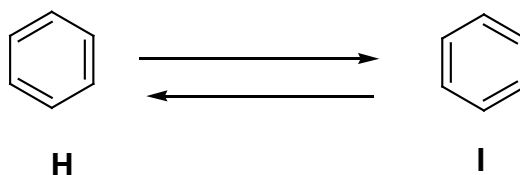
But is it true that structure **A** is fully satisfactory?

If we look at structure **A** with a keen eye we realize that two 1,2- dibromo isomers (**F** and **G**), differing in the positions of bromine in relation to the double bonds should be possible for structure **A**:

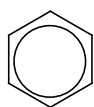


Kekulé visualized the benzene molecule in terms of two structures **H** and **I** between which the benzene molecule alternates.

Consequently the two 1,2- dibromobenzenes **F** and **G** would be in rapid equilibrium and thus could not be separated.



The two structures of benzene which are said to be in rapid equilibrium are what are now represented by the structure **J**. This is what is known as the resonance stabilized structure of benzene or hybrid structure



**J**

Which does not show alternate double and single bonds? This in fact is in agreement with the fact that the

bond lengths for C-C in benzene are all equal and that they are intermediate between single and double bonds. On what 3 premises did Kekulé base his reasoning?:

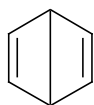
1. Benzene is  $C_6H_6$ .
2. All the hydrogens of benzene are equivalent.
3. The structural theory requires that there be four bonds to each carbon



## Formative evaluation

Qn 1. What are the necessary features for a compound to be aromatic?

Qn. 2. A number of structures have been proposed as possible structures for benzene, for example the so called Dewar structure below



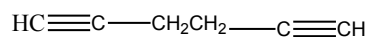
Dewar structure of benzene

How many monosubstitution products would this give if for example one hydrogen were replaced by bromine?

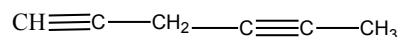
3. The following compounds A-D have the formula  $C_6H_6$ .

(i) for which of these compounds, if any, would substitution of bromine yield only one monobromo product?

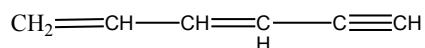
(ii) Which of these would you expect to react with bromine by substitution only? support your answer by giving convincing arguments



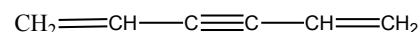
A



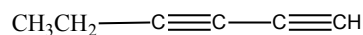
B



C



D



E

**Sample answer to part (ii) above:** All the above compounds are aliphatic and have multiple bonds (double bonds and/or triple bonds). Therefore all of them are capable of undergoing addition reactions across the multiple bonds. The answer is therefore none of these compounds would react with bromine by substitution alone.



## Learning activities

1. Read the chapter on aromaticity in Virtual Organic Chemistry by William Reuch. Follow the arguments given on the nature of reactions of benzene (pay special attention to the following:

- that despite the high unsaturation of benzene, it does not undergo addition reactions as alkenes or cycloalkenes do
- that one and only one monosubstitution product is possible for benzene
- that there can be only three disubstituted benzenes e.g. three dibromobenzenes. Draw the structures of the dibromobenzenes and name them using the IUPAC system.

2., the story or history of the structure of benzene is such that it warrants writing a well arranged argument on how its structure was arrived at.

Write an essay on the structure of benzene. Start with the fact that its molecular formula is  $C_6H_6$  and argue to arrive at the Kekulé structure. Show clearly how other acyclic and cyclic structures fail to qualify based on the possible isomer number of mono and disubstituted benzene derivatives. You may discuss with a colleague first then you should each write the essay on your own and later compare notes.

**All this can easily be done through e-mail via attachment. You can give each other comments so as to improve your understanding of the subject matter. You may also decide to chat through internet.**



## Learning activity # 2

**Title of Learning Activity :** Benzene and its derivatives

### Summary of the learning activity

Unit II: Benzene and its derivatives

- (a) do practice problems related to the possible isomer number for mono and disubstituted benzene derivatives from Organic chemistry practice problems text book by William Reusch
- (b) name different benzene derivatives using the IUPAC system of nomenclature
- (c) carry out qualitative and quantitative exercises on electrophilic aromatic substitution reactions of benzene and its derivatives
- (d) do practice problems related to the effects of different substituents present in benzene ring on the reactivity of the ring and orientation of incoming group to the ring.
- (e) perform hands-on experiments involving different electrophilic substitution reactions of benzene derivatives under laboratory conditions. . For this, open learning institutions are encouraged to arrange practical sessions with other learning institutions which have facilities. This is normally the practice with open universities eg the Open University of Tanzania (OUT).
- (f) do hands-on synthetic reactions involving transformation of benzene derivatives into simple industrially important molecules eg simple azo dyes (same as (e) above)

### Key words

IUPAC nomenclature  
Benzene derivatives  
Substituent  
Electrophilic aromatic substitution  
Reactivity and orientation



### List of relevant readings

FromTextbook Revolution-Taking the Bite out of Books

**<http://textbookrevolution.org/chemistry/>**

1. Virtual Textbook of Organic ChemistryOrganic Chemistry by William Reusch
2. Organic Chemistry by Richard and Sally Daley
3. Organic Chemistry Practice Problems by William Reusch

### List of relevant resources

List of relevant useful links : [http://anchem.umu.es/cgi\\_bin/pointer.exe?](http://anchem.umu.es/cgi_bin/pointer.exe?)

Demonstration

Isolation of caffeine from tea:-

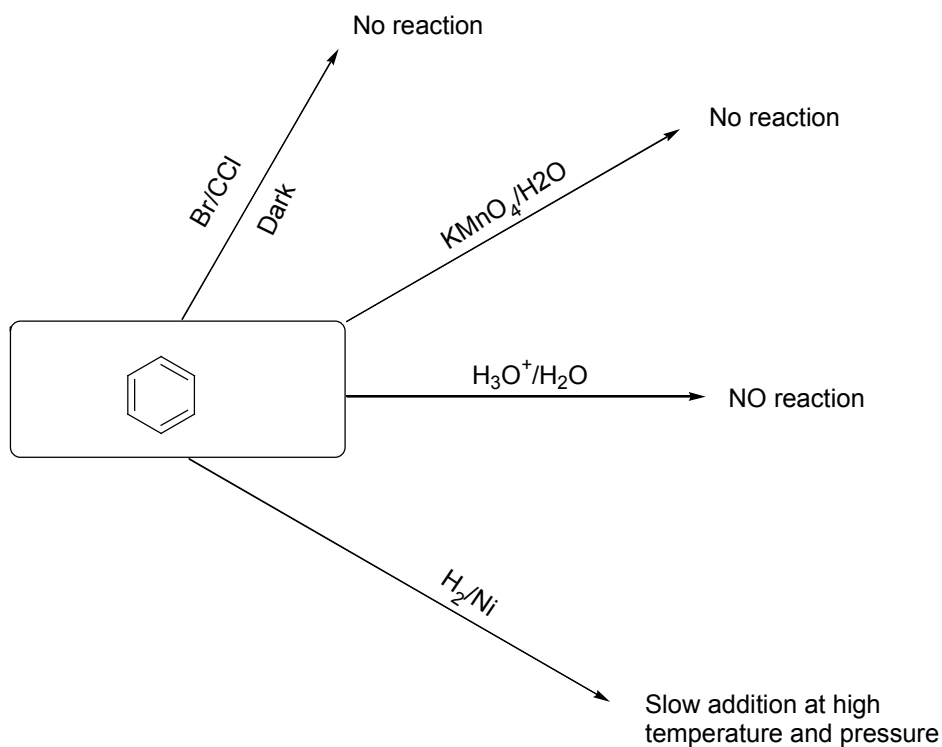
A microscale experiment using one or more tea bags and clean dichloromethane, extraction of the caffeine from water



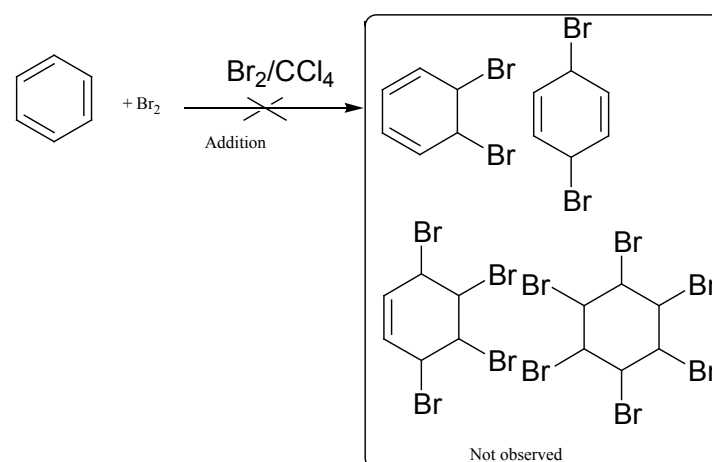
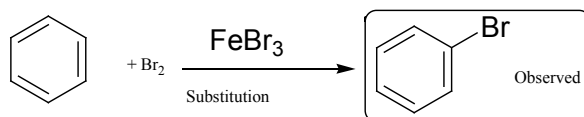
## Detailed description of the activity

### Reactions Of Benzene

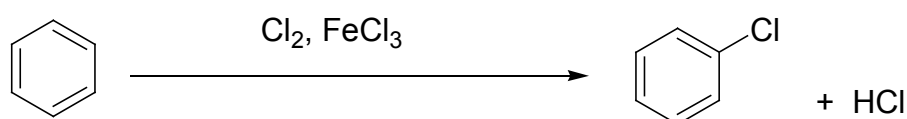
Benzene is an unsaturated hydrocarbon. One would expect it to undergo addition reactions typical of unsaturated compounds such as. the decolorizing of bromine in carbon tetrachloride, the decolorizing of potassium permanganate by oxidation, that it would undergo hydrogenation in the presence of a catalyst easily. In fact benzene does none of these.



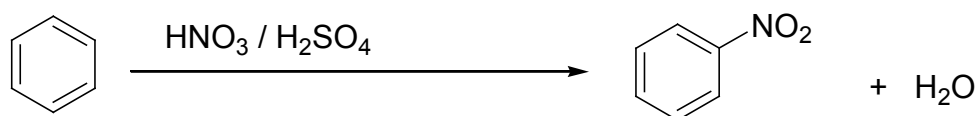
Surprisingly benzene does react with bromine but only in the presence of a Lewis acid catalyst such as ferric bromide; however, it undergoes substitution reaction rather than addition



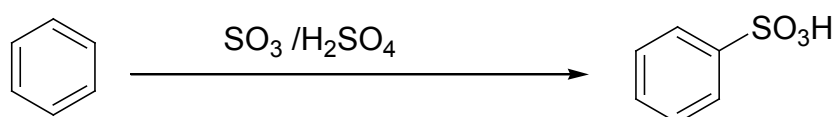
Benzene undergoes similar substitution reactions with chlorine in the presence of (i) ferric salt,



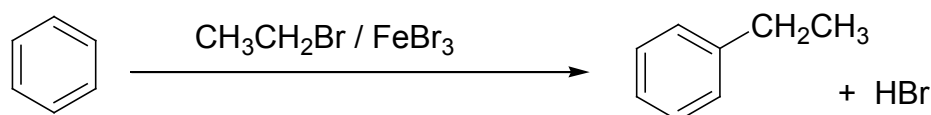
(ii) with nitric acid in the presence of sulphuric acid,



(iii) with  $\text{SO}_3$  in the presence of sulphuric acid and



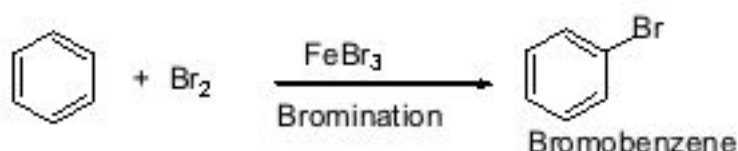
(iv) with an alkyl halide in the presence of aluminium chloride



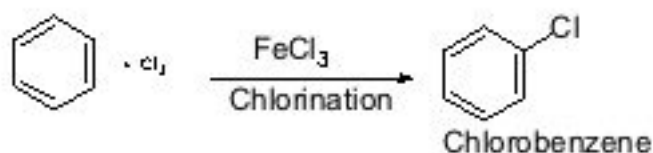


## MOST IMPORTANT ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS OF BENZENE

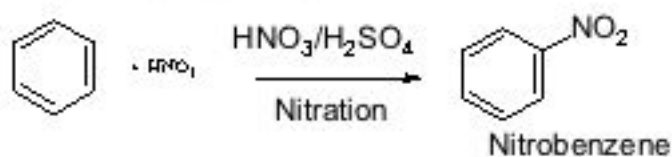
### Bromination of benzene



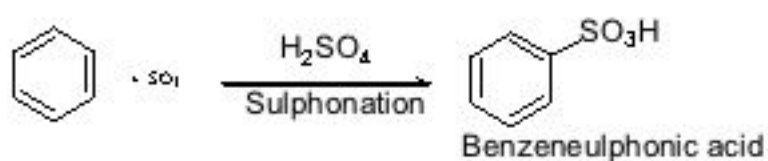
### Chlorination of benzene



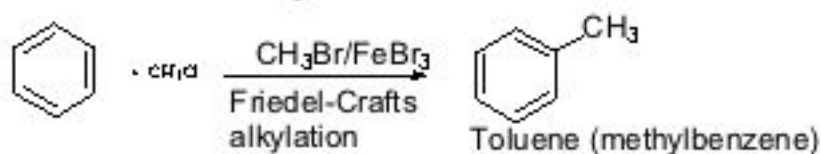
### Nitration of benzene



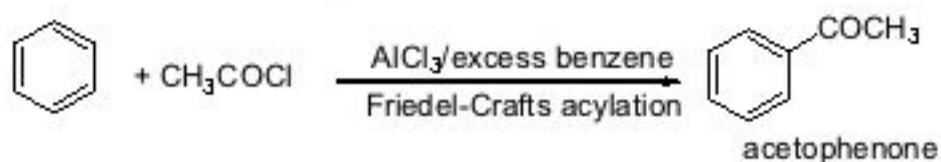
### Sulphonation of benzene



### Friedel-Crafts alkylation of benzene



### Friedel-Crafts acylation of benzene



### Nitration of benzene



Nitrobenzene
 Aniline (aminobenzene),  
a primary amine

Nitration

reduction

$\text{SnCl}_2/\text{HCl}$  (cold)

Diazotization

benzenediazonium salt

coupling with

p-methylphenol  
p-cresol

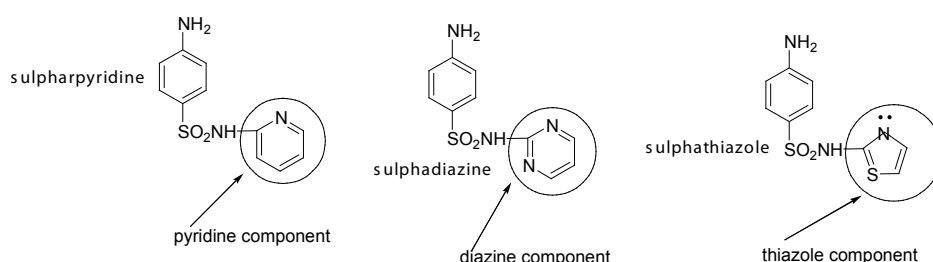
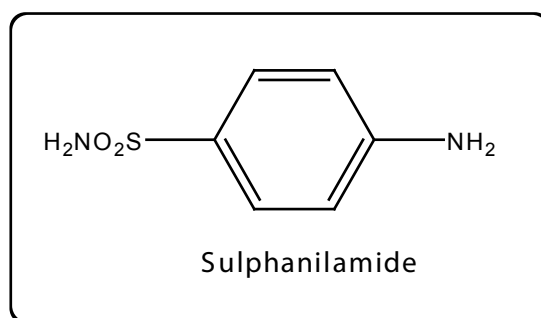
4-Methyl-2-(phenylazo)phenol

An azo dye



## Sulphonation of benzene

Aromatic sulphonic acids are important intermediates in the preparation of industrially important molecules such as dyes and pharmaceuticals. For example, the long time antibiotic sulphanilamide is one of many sulphur drugs which involve a sulphonation step in its manufacture. As the name implies many of these sulphur drugs are amides of aromatic sulphonic acid, thus the precursors for sulphur drugs are aromatic amines and aromatic sulphonic acids, compounds which originate from nitration and sulphonation of benzene or its derivatives. Sulphanilamide has chemotherapeutic effect against many diseases including the deadly killer diseases in Africa, like cholera. There are now many analogues of sulphanilamide which have even better chemotherapeutic effects but all in all they all depend on electrophilic substitution reaction of benzene and its derivatives. Here are some examples of such drugs:



## Reactions of substituted benzene derivatives

Benzene reacts with electrophiles (species which are poor in electrons) because itself is rich in electrons due to its easily accessible  $\pi$ -electron system. If benzene has another group attached to it, its reactivity will be changed depending on the nature of that group. If it is an electron rich group, one which can donate electrons to the benzene ring, then the benzene derivative will be more reactive

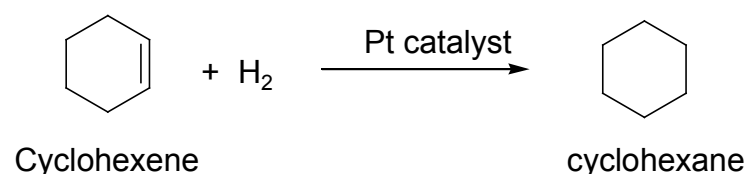


towards electrophilic aromatic substitutions than benzene itself. If the group is electron-poor, one which tends to withdraw electrons from the benzene ring then the benzene derivative will be less reactive than benzene. Substituents that make the benzene ring more reactive are called activating groups or **activators**, and those substituents that make the ring less reactive are called deactivating groups or **deactivators**. Activators are normally have electron donating effect to the ring either by resonance or by induction while deactivators have electron withdrawing effect. In addition to activating and deactivating effects, the presence of a substituent on the ring has a second effect, that of orienting an incoming group to go to a particular position on the ring. Substituents are subdivided into two groups in this sense, there are those that direct incoming groups to the ortho and para positions and those that direct incoming groups to the meta position. So we have the so called **ortho-para directors** and **meta directors**. Except for a few exceptions eg the halogens, normally the **activating** groups are **ortho-para directors** while **deactivating** groups are **meta directors**. Except the halogens which are **deactivating** but **ortho-para directors**.

### The Stability Of Benzene

We have seen in unit I of this module that benzene is unusual in its behaviour in that it undergoes substitution reactions rather than addition reactions expected of it on the basis of its Kekule' structure. Benzene is also unusual in its stability, it is more stable than what the Kekule' structure suggests. Let us consider the following:

Cyclohexene, a six-membered ring containing one double bond, can be hydrogenated to cyclohexane and generate 120 kJ/mole, so much like that of any alkene.



$$\Delta H^\circ = -120 \text{ kJ / mol}$$

We would expect that hydrogenation of 1,3-cyclohexadiene would liberate roughly twice as much heat and thus have  $\Delta H^\circ = 240 \text{ kJ/mol}$ . Experimentally the result is -232 kJ/mol which is quite close to the calculated value. The difference can be explained by taking into account that compounds containing conjugated double bonds are usually more stable than isolated double bonds.

If we extend this thinking and consider benzene to be 1,3,5-cyclohexatriene, we would expect that benzene should liberate approximately thrice as much energy



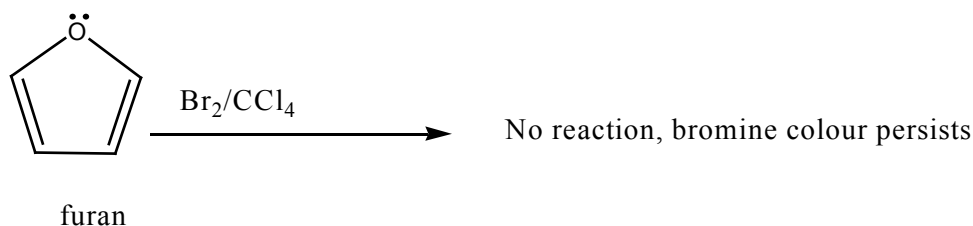
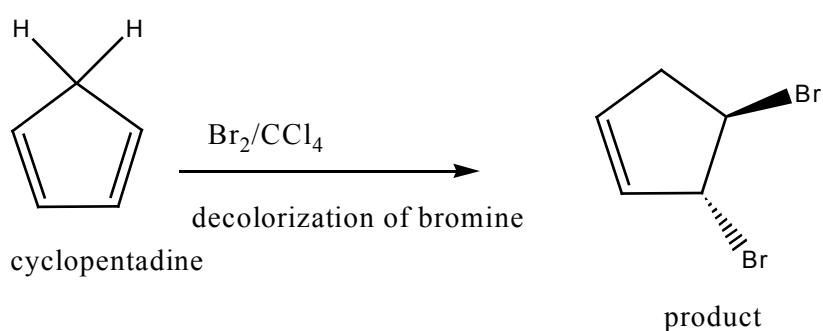
as that of cyclohexene i.e.  $(3 \times -120) = -360 \text{ kJ/mol}$ . Experimentally, however, the amount of energy liberated by benzene is surprisingly different. The reaction is exothermic alright but the amount liberated is  $150 \text{ kJ/mol}$  less than expected. Thus benzene is more stable than the hypothetical 1,3,5-cyclohexatriene by  $150 \text{ kJ/mol}$ . The difference between the amount of heat actually released and that calculated is what is referred to as the stabilization energy of the compound, in this case of benzene. This is also known as the **resonance energy** or the **delocalization energy**. Thus the resonance energy of benzene is  $150 \text{ kJ/mol}$ . It is a measure of how much more stable benzene is than would be predicted on the basis of its formulation as a pair of rapidly interconverting 1,3,5-cyclohexatrienes.



## Formative evaluation : Learning activities

Consider the following molecules:

Both cyclopentadiene and furan have each two double bonds, however when both are subjected to bromination in carbon tetrachloride this is the result:



Explain the above observation based on what you have learned so far.

### Learning activities: Simulation Experiment

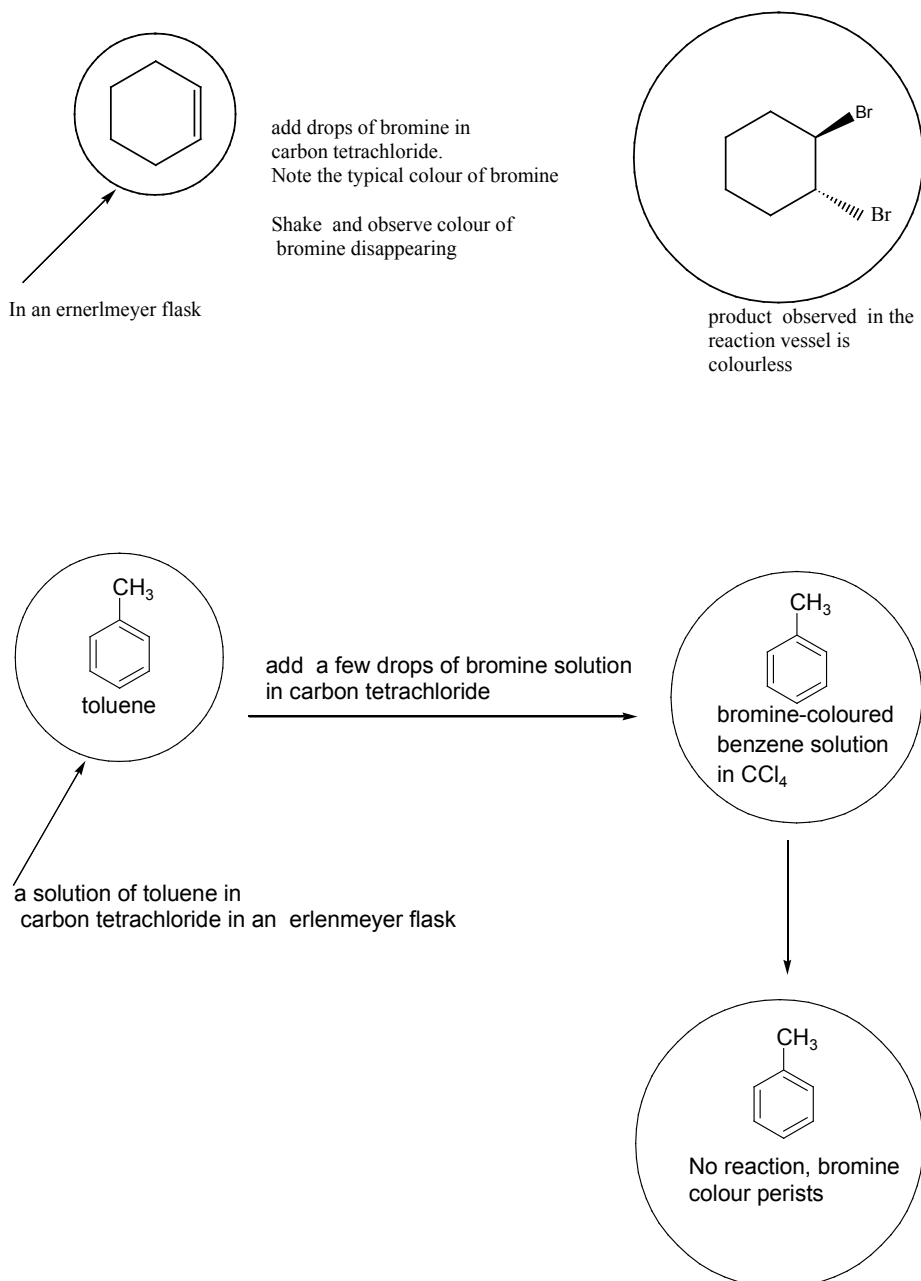
1. Perform a simulation experiment to show reaction of cyclohexene with  $\text{Br}_2$  in carbon tetrachloride
2. Perform another similar experiment using a similar set up but use toluene in stead of cyclohexene

Resources needed:

Bromine in carbon tetrachloride  
 Cyclohexene  
 Toluene  
 Pipette



The aim of this simulation is to demonstrate that unsaturated aliphatic hydrocarbons such as cyclohexene decolourize bromine because they undergo addition reaction easily to give the dibromo compound whereas unsaturated aromatic hydrocarbons eg toluene under identical conditions do not undergo addition reactions and the bromine colour persists.





## Learning activity # 3

**Title of Learning Activity :** HeterocyclicAromatic Compounds

### Summary of the learning activity

Unit III: Heterocyclic Compounds: These are aromatic compounds in which one or more of the carbons forming the ring has been replaced by a hetero atom eg O, N, or S

Typical examples of heterocyclic aromatic compounds

Electrophilic aromatic substitution reactions of furan, thiophene and pyrrole

Furan, thiophene, and pyrrole as examples of 5-member ring monoheterocyclics, Pyridine,quinoline

### Key words

Heterocyclic aromatic compound  
Electrophilic aromatic substitution  
a hetero atom  
5-member ring  
monoheterocyclic

### List of relevant readings

<http://en.wikipedia.org/wiki/Aromaticity>

### List of relevant resources

### List of relevant useful links

**Title :**Heterocyclic compounds

**URL :**

<http://www.cem.msu.edu/%7Ereusch/VirtualText/heterocy.html>  
(visited on 15th September 2006)

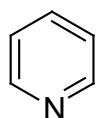


## Detailed description of the activity

### Heterocyclic aromatic compounds

Definition of heterocyclic aromatic compounds:

A heterocyclic compound is one in which all the atoms forming the cyclic system are not of the same type. Thus a heterocyclic aromatic compound is a cyclic aromatic compound with one or more atoms forming the ring other than carbon. One such example is pyridine in which one carbon of the benzene ring is replaced by nitrogen (see structure below):



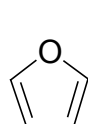
Pyridine

Benzene and its derivatives that we discussed in units I and II of this module are not heterocyclic because all the atoms that form the benzene ring are carbons.

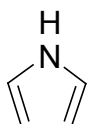
The most common hetero atoms in many heterocyclic aromatic compounds are oxygen, nitrogen and sulphur. Heterocyclic aromatic compounds are quite common in nature. Some of these natural heterocyclics appear in complex molecules such as DNA molecule, the molecule which is responsible for storage of genetic information, and RNA, the molecule involved in the synthesis of enzymes.

In this unit we are going to learn about simple heterocyclic aromatic molecules as representatives of this group of compounds, we will in particular, study the five member ring heterocyclics furan, pyrrole and thiophene. For the six member ring system we will study pyridine and quinoline, a fused ring system consisting of benzene and pyridine components.

The structures of furan, pyrrole, thiophene, pyridine and quinoline are shown in Kekulé form



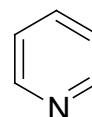
furan



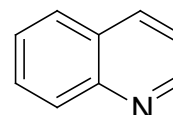
pyrrole



thiophene



pyridine

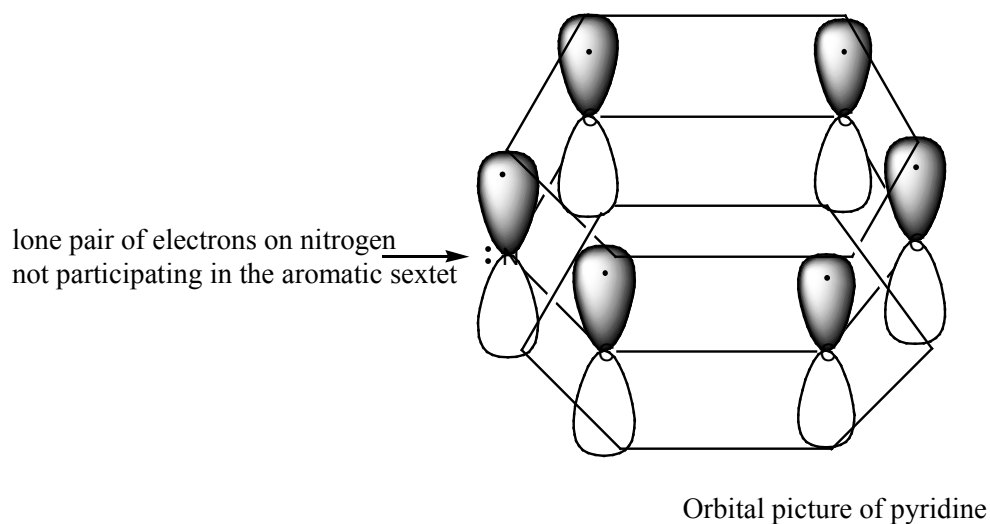
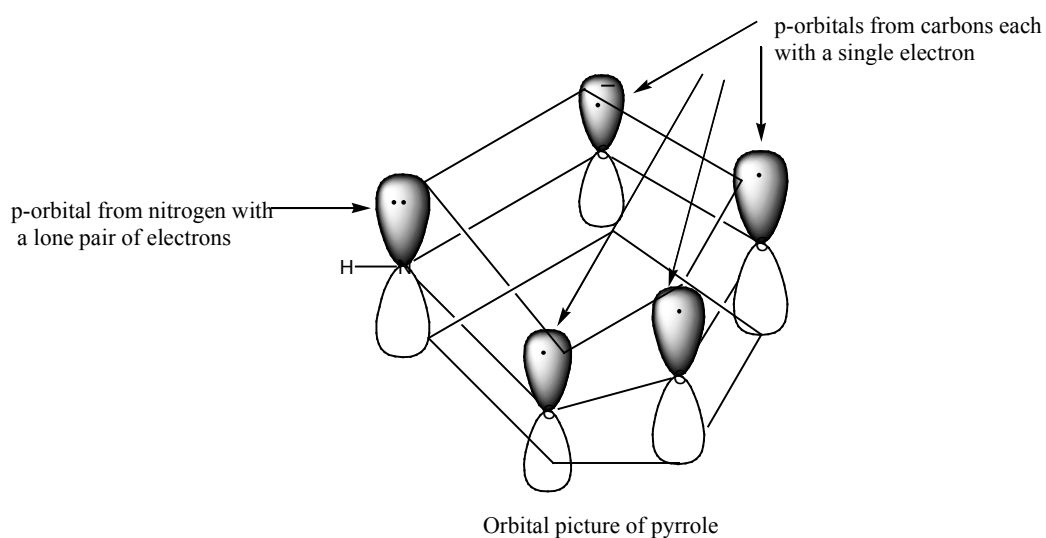


quinoline

Let us compare pyrrole, both with nitrogen as the hetero atom. In pyrrole the nitrogen does not have a double bond, therefore it does not contribute one pi electron as the case in pyridine where the nitrogen forms part of the conjugated system of the double and single bonds (see the orbital picture for pyrrole and



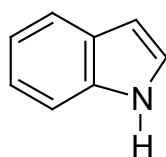
pyrrolidine below): The nitrogen in pyrrole contributes its lone pair of electrons which together with the 4 electrons from the p-orbitals of carbon form the sextet. Thus the p-orbital carrying the lone pair together with the p-orbitals from the four carbons, each with one electron overlap to make the six delocalized electrons. The orbital pictures for pyrrole and pyridine are as shown:





## Formative evaluation

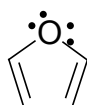
1. The following is the structure of indole,



Indole

Which aromatic rings that you know are the components of the fused ring system in indole? Hint: remember that quinoline is a fused ring system of benzene (a homocyclic) and pyridine (a heterocyclic), how about indole?

2. Observe the structure of furan:



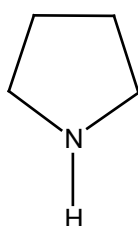
Furan has two double bonds only with four pi electrons. How do you explain the aromatic nature of furan based on the Huckel;  $4n+2$  Rule? How does it happen to have the desired number of pi electrons?

3. Both pyridine and pyrrole are aromatic molecules. How do you account for the fact that pyrrole is less basic than pyridine? (Hint consider the availability of the lone pair of electrons on nitrogen for protonation in each of the molecules)



## Learning activities

1. Draw the molecular orbital pictures for benzene, pyridine and thiophene. Which two of these are similar? Explain. How is the dissimilar molecule different from the two similar molecules?
2. Given below is the structure of pyrrolidine



pyrrolidine

Would you expect pyrrolidine to be more or less basic than pyrrole? Explain your answer.

3. If there is a possibility to have laboratory facilities do the following: Dissolve pyridine, pyrrole and pyrrolidine in HCl in three different test tubes and make your observations. Clearly explain your results based on your knowledge of this module. This question is only for those students who have access to laboratory facilities.



## XV. Synthesis of the Module

**Unit 1 introduces the concept of Aromaticity** and examines the properties of aromatic compounds:

Aromaticity is a property of ring compounds with a continuous conjugated system of double and single bonds.

Aromatic molecules are planar and have a total number of  $\pi$ -electrons equal to  $4n+2$  electrons where  $n$  is an integer 0,1,2 3..... Thus molecules must have 2,6,10,14,18,22.....etc  $\pi$ -electrons for them to qualify as aromatic. This is the so called Huckel's  $4n+2$  rule on aromaticity

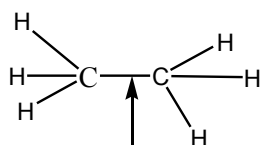
Aromatic compounds have unusual stability as unsaturated compounds. They typically undergo electrophilic aromatic substitution reactions rather than addition reactions typical of unsaturated aliphatic compounds.

Benzene and its derivatives are typical examples of aromatic compounds.

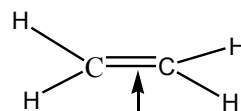
**Unit 2 discusses Benzene and its derivatives:**

The formula for benzene is  $C_6H_6$  or  $(CH)_6$ . It has double bond equivalent of 4 (this is also known as index of hydrogen deficiency). Being a six-member ring, benzene then must have three double bonds as per Kekulé structure to satisfy the index of hydrogen deficiency.

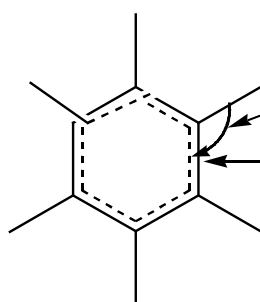
The Kekulé structure shows benzene to have three double bonds, but benzene is far from being a 1,3,5-cyclohexatriene. It does not undergo addition reactions, its C-C bond lengths are all equal *vis* 0.139 nm, intermediate between single and double bonds.



C-C bond length in ethane is 0.154 nm



C=C bond in ethene is 0.134 nm



Bond angle is  $120^\circ$   
(all angles are equal)

Bond length of benzene 0.139 nm  
(all bonds are equal)

Its bond angles are all  $120^\circ$

Only one monosubstituted derivative is possible and only three disubstituted isomers are possible i.e. the 1,2- (ortho isomer), 1,3- (meta isomer) and 1,4- (para isomer).

Typical reactions of benzene are electrophilic aromatic substitutions such as bromination, nitration, sulphonation and Friedel-Crafts reactions (alkylations and acylations).

**Unit 3: extends the concept of aromaticity and discusses five-member ring heterocyclic compounds-** Heterocyclic aromatic compounds. Typical examples discussed in this unit are the five-member ring monoheterocyclics furan, pyrrole and thiophene with oxygen, nitrogen and sulphur as the heteroatoms respectively; and pyridine as a six member ring heterocyclic with nitrogen as the heteroatom.

Heterocyclics are important components in many natural products and are of immense importance in pharmaceuticals.

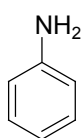
Heterocyclic aromatic compounds, as their benzenoid counterparts, have unusual stability, and undergo typical electrophilic aromatic substitution reactions rather than addition reactions.



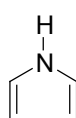
## XVI. Summative Evaluation

### Questions:

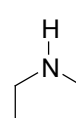
1. Which of the following compounds is least basic? (Hint: In this case basicity is a measure of how easily accessible the lone pair of electrons on nitrogen is for protonation.



A



B

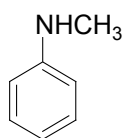


C

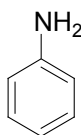


D

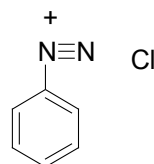
2. Which of the following compounds is the most immediate precursor (please use a phrase that is accessible to the beginning learner) for an azo dye?



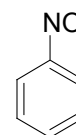
A



B

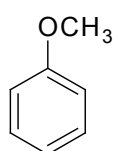


C

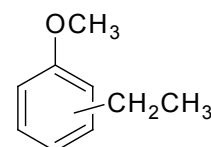


D

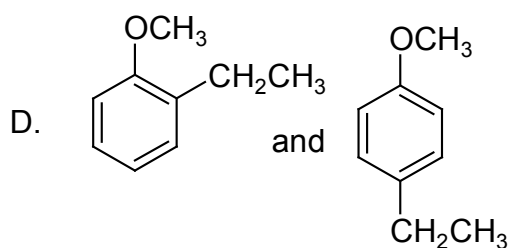
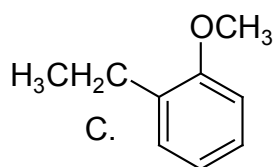
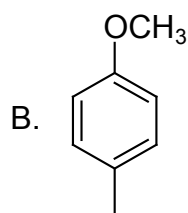
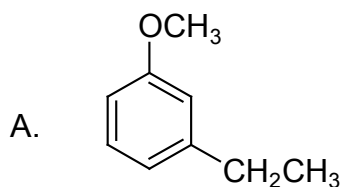
3. Consider Friedel/Crafts reaction of the following:



Friedel/Crafts reaction,  $\text{CH}_3\text{CH}_2\text{Cl}/\text{AlCl}_3$



The possible structure(s) of the product(s) is/are



4. For a compound to be aromatic it must be planar because if the compound is not planar or at least quite close to planar
  - A. its electrons cannot form an aromatic sextet
  - B. the 2p orbitals do not overlap well and some connectivity between orbitals is lost
  - C. there is far better overlap of the p-orbitals
  - D. it cannot have  $4n+2$   $\pi$ -electrons
  
5. Aromatic systems contain  $4n+2$   $\pi$ -electrons where n is
  - A. the number of carbon atoms in the ring,
  - B. the number of lone pairs of electrons in the molecule
  - C. an integer excluding zero
  - D. an integer.



6. When benzene undergoes electrophilic aromatic substitution reaction such as bromination the benzene molecule acts as
- an electrophile
  - a nucleophile
  - an electron acceptor
  - none of the above options is correct
7. When benzene undergoes nitration using a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  the nitrating agent in this reaction is
- $-\text{NO}_3$
  - $-\text{NO}_2^+$
  - $-\text{NO}$
  - $-\text{NO}_2$
8. In Friedel/Crafts reaction of benzene, it is important to have a Lewis acid because the Lewis acid
- the neutralizes the basic reaction mixture
  - makes the alkyl halide a better electrophile
  - polarizes the C-X bond and thus facilitate the electrophilic attack by benzene
  - B and C above are both correct.
9. Which of the following are all activating groups towards electrophilic aromatic substitution reactions:
- $\text{CH}_3\text{O}-$ ,  $-\text{OH}$ ,  $-\text{CH}_3$ ,  $-\text{Br}$
  - $-\text{NH}_2$ ,  $-\text{NHCH}_3$ ,  $-\text{COCH}_3$ ,  $\text{C}\equiv\text{N}$
  - $\text{Et}_3\text{N}-$ ,  $\text{PhNH}-$ ,  $\text{CH}_3\text{CH}_2-$ ,  $\text{PhO}-$
  - $\text{Br}-$ ,  $\text{Ph}-\text{C}(=\text{O})-$ ,  $\text{H}-\text{C}\equiv\text{C}-$ ,  $\text{EtO}-$



10. The heat of hydrogenation of 1,3,5,7-cyclooctatetraene (COT) is about 420 kJ/mol, whereas the heat of hydrogenation of cyclooctene is about 100 kJ/mol. This is because
- A. COT has aromatic characteristics
  - B. both COT and cyclooctene are aromatic
  - C. both COT and cyclooctene undergo typical substitution reactions
  - D. almost each double bond in COT behaves as an isolated double bond

11. Which of the following is the correct statement::

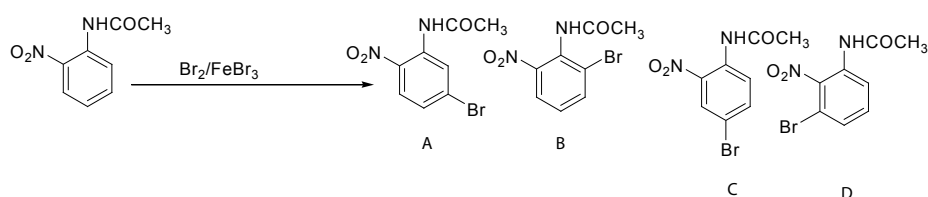
An electrophile is

- A. rich in electron density
- B. deficient of electrons
- C. seeks electrons
- D. B and C are both correct

12. When benzene undergoes its typical reactions it behaves as

- A. an electron donor
- B. an electron acceptor
- C. an electrophile
- D. non of the above is correct

13. Which is the most likely major product in the following reaction:





**14.** When anisole (methoxybenzene) is chlorinated the products are 65% 1,4-product and 34.9% 1,2- product. The predominance of the 1,4 product ( para-isomer) over the 1,2-Product (ortho- isomer) is most likely due to the fact that

- A. the methoxy group directs the chloro group mostly to the para position
- B. the methoxy group prefers the para isomer
- C. the 1,2 isomer is less preferred due to steric hinderance
- D. the methoxy group pushes electrons (by resonance) more to the para position

**15.** In nitration of p-nitrotoluene the major product is 2,4-dinitrotoluene due to

- A. the directing effect of the methyl group
- B. the directing effect of the nitro meta director
- C. the combination of the activating and deactivating effects of the two groups
- D. the directing effects of both the ortho-para director and the meta director

15 X 4 marks = 60 marks



**Answers:**

1. B
2. C
3. D
4. B
5. C
6. B
7. B
8. D
9. C
10. D
11. D
12. A
13. C
14. C
15. D



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